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FORMING THE COMPETENCY BASED EDUCATION MODULES FOR CHEMICAL ACCIDENT PREVENTION, PREPAREDNESS AND RESPONSE

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REPUBLIC OF TURKEY
Minister for EU Affairs
Turkish National Agency

FORMING THE COMPETENCY BASED EDUCATION MODULES FOR CHEMICAL ACCIDENT PREVENTION, PREPAREDNESS AND RESPONSE

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Forming the Competency Based Education Modules for Chemical Accident Prevention, Preparedness and Response

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PREFACE

With rapid growth in modern technologies is increasing use of chemical substances within industry and trade. It is estimated that a large number of people could endanger life in a possible accident resulting from the use of these substances. This situation, under technological disasters can bring risks in terms of countries. At the same time, managing the resulting risk requires a serious approach and expertise.

In order to be successful in the search and rescue works in chemical disasters, it is necessary to use modern instruments in parallel with the modern technological advancements, to carry out these works in a planned and coordinated way using well trained professional search and rescue teams, to improve the efficiency of the institutions of vocational education and to increase the cooperation among universities, SMEs, companies, research and development centres and other stakeholders.

We can summarize general information of the project prepared in this frame as follows.

Name of the project is "Forming The Competency Based Education Modules for Chemical Accident Prevention, Preparedness and Response". The project is the Ministry of the European Union, the European Union Education and Youth Programs Center, Erasmus + Programme Home Action 2 within the scope of Vocational Training Strategic Partnership. It was adopted with the Project Number 2015-1-TR01- KA202-021323 on 2015.

Main actor in the project is Karabuk Disaster and Emergency Directorate. The project partners are KARDEMİR Co., Karabuk University, HAMK University, LAMK University, Previform Lda and Tesicnor Lda. All partners are working as a specialist in their fields.

Main activity of the project is the strategic partnership. At the project, it is aimed at better quality education and innovative practices that can lead to institutional modernization. In addition, it is aimed to transfer, apply, test and disseminate the field knowledge / skills and abilities by bringing together related institutions / organizations. In particular, the aim of the project is to create a new profile and develop a Training Modules for professionals working specific sectors such as Security, Health, Emergency, Crisis Management Search and Rescue.

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LIST OF SYMBOLS

kPa	Kilopascal is a unit of pressure.
°C	the Celsius scale of temperature.
Σ	Summation - sum of all values in range of series.
ppmV	Parts per million by volume.
ppm	This is an abbreviation for "parts per million.

LIST OF ABBREVIATIONS

AFAD	Disaster and Emergency Management Presidency.
CAS	Chemical Abstract Service.
ChemiPPR	Forming the Competency Based Education Modules for Chemical Accident Prevention, Preparedness and Response.
CLP	Classification, Labelling and Packaging of Substances and Mixtures.
CMR	Chemicals classified as carcinogenic, mutagenic or toxic to reproduction under Directive 67/548 (see 'legislation').
CSTEE	Scientific Committee on the Toxicity, Ecotoxicity and the Environment of the Commission.
ECVAM	the JRC's European Centre for the Validation of Alternative Methods.
ELINCS	European List of Notified Chemical Substances.
EINECS	European Inventory of Existing Commercial Chemical Substances.
GHS	Globally Harmonized System of Classification and Labelling of Chemicals.
ICCA	International Council of Chemical Associations**.**
ICE	Europe the International Chemical Environment.
IFCS	Intergovernmental Forum on Chemical Safety.
ILO	International Labour Organisation.
IUCLID	International Uniform Chemical Information Database.
JRC	Joint Research Centre of the Commission.
LPV	Low Production Volume chemicals.
NGOs	Non-governmental organisations representing particular stakeholders' interests (e.g. consumers, environment).

NIOSH	The National Institute for Occupational Safety and Health.
OECD	Organisation for Economic Co-operation and Development.
OSPAR	Oslo - Paris Convention for the Protection of the Marine Environment of the North East Atlantic.
PBT	Persistent, bio-accumulative and toxic chemicals.
POCP	Photochemical ozone creation potential.
POPs	Persistent Organic Pollutants.
PPE	Personal Protective Equipment
QSAR	Quantitative Structure Activity Relationship. Models used to predict the properties of chemicals from the molecular structure.
REACH	Registration, Evaluation and Authorisation of Chemicals.
SIDS	Screening Information Data Set (SIDS) outlining the minimum data elements for determining whether an existing HPV chemical requires further investigation in the OECD's HPV/ICCA programme.
SMEs	Small to medium size enterprises employing less than 250 workers.
UN	United Nations.
UNCED	UN Conference on Environment and Development at the 1992 Earth Summit in Rio.
VPVB	Very persistent and very bio-accumulative chemicals.
WHO	World Health Organisation.

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LIST OF TERMS

Abiotic Resources: Resources which are considered abiotic and therefore not renewable. Zinc ore and crude oil are examples of abiotic resources.

Ancillary Material: Material that is not used directly in the formation of a product or service.

ADN: The European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways annexed to resolution No: 223 of the Inland Transport Committee of the Economic Commission for Europe, as amended.

ADR: The European Agreement concerning the International Carriage of Dangerous Goods by Road under framework Directive 94/55/EC, as amended

Aerosols: Aerosol dispensers, any non-refillable receptades made of metal, glass or plastics and containing a gas pressed, liqcomuefied or dissolved under pressure with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in gas, as a foam, paste or powder or in a liquid state or in gaseous state.

Alloy: A metallic material, homogeneous on a macroscopic scale, consisting of two or more elements so combined that they cannot be readily separated by mechanical means; alloys are considered to be mixtures for the purposes of CLP.

Article (under REACH and CLP): An object which during production is given a special shape, surface or design which determines its function to greater degree than does its chemical composition.

Aspiration: The entry of liquid or solid chemical substances or mixture into the trachea and lower respiratory system directly through the oral or nasal cavity, or indirectly from vomiting.

Biotic Resources: Resources which are considered biotic and therefore renewable. The rainforests and tigers are examples of biotic resources.

Bund: Means a wall, which may form part of the perimeter of a compound, designed to contain spills of liquids – both the bund and the compound floor must be sufficiently impervious to retain spillage or leakage.

Carcinogen: A substance or mixture of substances which includes cancer or increases its incidence.

CLP or CLP Regulation: Regulation (EC) No 1272/ on Classification, Labelling and Packaging of Substances or a Mixtures.

Competent Authority: The authority or authorities or bodies established by the Member States to carry out the obligations arising from the CLP Regulation.

Compatible: In relation to two or more substances, means the substances will not react together to cause, or substantially increase the likelihood of, a serious incident.

Consequence: Outcome of an event affecting objectives.

Note 1 to entry: An event can lead to a range of consequences.

Note 2 to entry: A consequence can be certain or uncertain and can have positive or negative effects on objectives.

Note 3 to entry: Consequences can be expressed qualitatively or quantitatively.

Note 4 to entry: Initial consequences can escalate through knock-on effects.

Consequence Distance: The distance from the hazard, within which damage or injury can be expected (to life, health, the environment, or assets) due to the accident.

Containers and Packages: Any movable equipment used to store, transport, treat, or dispose of hazardous materials. Containers or packages include all types of mobile methods used for hazardous materials.

Control: Measure that is modifying risk.

Note 1 to entry: Controls include any process, policy, device, practice, or other actions which modify risk.

Note 2 to entry: Controls may not always exert the intended or assumed modifying effect.

Critical Event: This term is commonly defined as the event causing a loss of containment (LOC). This definition is quite accurate for fluids, as they usually behave dangerously after release. For solids and more especially for mass solid storage, the term “loss of physical integrity” (LPI) is considered more appropriate, as the critical event in this case is the change of chemical and/or physical state of the substance. The critical event is the centre of the bow-tie

Corrosive to Metals: Materially damaging or even destroying, metals by chemical action of a substance or a mixture.

Damage: A deterioration in the quality of the environment not directly attributable to depletion or pollution.

Danger Means: a signal Word indicating the more severe hazard categories.

Dangerous Substance, Hazardous Materials, Dangerous Goods, Hazardous Chemicals: A substance that can be biological, chemical, or physical and has the potential to cause harm to humans, animals, plants, or the environment either by itself or by interacting with another material or factor (e.g., water, temperature change).

Distributor: Any natural or legal person established within the Union, including aretailer, who only stores and places on the market a substance, on its own or in mixture, for third parties.

Downstream User: Any natural or legal person established within the Union, other than the manufacturer or the importer, who uses a substance, either on its own or in a mixture, in the course of his industrial or professional activities.

Detection: The means of detection of the failure mode by maintainer, operator or built in detection system, including estimated dormancy period (if applicable).

Depletion: The result of the extraction of abiotic resources (non-renewable) from the environment or the extraction of biotic resources (renewable) faster than they can be renewed.

Eco-Efficiency: The relationship between economic output (product, service, activity) and environmental impact added caused by production, consumption and disposal.

Emission: One or more substances released to the water, air or soil in the natural environment.

End Effect: The failure effect at the highest indenture level or total system.

Environment: Surroundings in which an organization operates, including air, water, land, natural resources, flora, fauna, humans, and their interrelations. This definition extends the view from a company focus to the global system.

Environmental Aspects: Elements of an organization's activities, products or services which can interact with the environment. A significant environmental aspect is an environmental aspect which has or can have a significant environmental impact.

Environmental Effect: Any direct or indirect impingement of activities, products and services of an organization upon the environment, whether adverse or beneficial. An environmental effect is the consequence of an environmental intervention in an environmental system.

Environmental Effects Evaluation: A documented evaluation of the environmental significance of the effect of an organization's activities, products and services (existing and planned) upon the environment.

Environmental Impact: Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organization's activities, products or services. An environmental impact addresses an environmental problem.

Environmental Impact Added: The total of all environmental interventions of a product or production system evaluated (weighted) according to the harmfulness of each intervention to the environment.

Environmental Intervention: Exchange between the economy and the environment including resource extraction, emissions to the air, water, or soil, and aspects of land use. If resource extraction is excluded, the term used in this case is environmental release.

Environmental Inventory: An environmental inventory identifies and quantifies - where appropriate - all environmental aspects of an organization's activities, products and services.

Environmental Issue: A point or matter of discussion, debate, or dispute of an organization's environmental aspects.

Environmental Management: Those aspects of an overall management function (including planning) that determine and lead to implementation of an environmental policy.

Environmental Performance: Measurable results of an environmental management system, related to the control of its environmental aspects. Assessment of environmental performance is based on environmental policy, environmental objectives and environmental targets.

Environmental Performance Index: A parameter describing environmental impact with a single figure. An index is usually calculated by weighting the actual impact level against a target level.

Environmental Performance Indicators: Different parameters describing the potential impact of activities, products or services on the environment. These parameters are the result of characterizing classified environmental interventions/environmental aspects.

Environmental Problem: An environmental problem is a description of a known process within the environment or a state of the environment which has adverse effects on the sustainability of the environment including society. They include resource consumption and environmental impacts.

Event: Occurrence or change of a particular set of circumstances.

Note 1 to entry: An event can be one or more occurrences, and can have several causes.

Note 2 to entry: An event can consist of something not happening.

Note 3 to entry: An event can sometimes be referred to as an “incident” or “accident”.

Note 4 to entry: An event without consequences can also be referred to as a “near miss”, “incident”, “near hit” or “close call”.

Explosive Article: An article containing one or more explosive substances.

Explosive Substance: A solid or liquid substance which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases.

Eye Irritation: The production of changes in the eye following the application of test substance to the anterior surface of the eye, which are fully reversible within 21 days of application.

Failure: The loss of a function under stated conditions.

Failure Mode: The specific manner or way by which a failure occurs in terms of failure of the item (being a part or (sub) system) function under investigation; it may generally describe the way the failure occurs. It shall at least clearly describe a (end) failure state of the item (or function in case of a Functional FMEA) under consideration. It is the result of the failure mechanism (cause of the failure mode). For example; a fully fractured axle, a deformed axle or a fully open or fully closed electrical contact are each a separate failure mode.

Failure Cause and/or Mechanism: Defects in requirements, design, process, quality control, handling or part applications, which are the underlying cause or sequence of causes that initiate a process (mechanism) that leads to a failure mode over a certain time. A failure mode may have more causes. For example; "fatigue or corrosion of a structural beam" or "fretting corrosion in an electrical contact" is a failure mechanism and in itself (likely) not a failure mode. The related failure mode (end state) is a "full fracture of structural beam" or "an open electrical contact". The initial cause might have been "Improper application of corrosion protection layer (paint)" and /or "(abnormal) vibration input from another (possibly failed) system".

Failure Effect: Immediate consequences of a failure on operation, function or functionality, or status of some item. Indenture levels (bill of material or functional breakdown) an identifier for system level and thereby item complexity. Complexity increases as levels are closer to one.

Flammable Gas: A gas having a flammable range with air at 20°C and a standard pressure of 101.3 kPa.

Flammable Liquid: A liquid having a flash point of not more than 60°C. Flash point means the lowest temperature at which the application of an ignition source causes the vapours of a liquid to ignite under specified test conditions.

Flash Point: The minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.

Gas: A substance which at 50°C has a vapour pressure greater than 300 kPa; or is completely gaseous at 20°C at a standard pressure of 101.3 kPa.

GHS: The “GloballyHarmonized System of Classificationa Labelling of Chemicals” developed within the United Nations (UN) structure.

Hazard: Anything, activity, occurrence or circumstance of any kind that has the potential to cause injury to persons or damage to property by an explosion, fire, harmful reaction or the evolution of flammable, corrosive or toxic vapours involving dangerous goods, or the escape, spillage or leakage of any dangerous goods.

Hazard Category: The division of criteria within each hazard class, specifying hazard severity.

Hazard Class: The nature of the physical, health or environmental hazard.

Hazard Identification Number: Indicates the danger of hazardous chemical.

Hazard Pictogram: A graphical composition that includes a symbol plus other graphic elements, such as a border, background pattern or colour that is intended to convey specific information.

Hazard Statement: A phrase assigned to a hazard class and category that describes the nature of the hazards of a hazardous substance or mixture, including where appropriate, the degree of hazard.

Hazardous: Fulfilling the criteria relating to physical hazards, health hazards or environmental, laid down in parts of CLP.

Hazardous Material: Dangerous chemical, dangerous goods.

Import: The physical introduction into the customs territory of the Union.

Importer: Any naturalor legal person established within the Union who is responsible for import.

Incompatible: Means those substances that are not compatible. See the definition of compatible.

Intermediate: A substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance.

IMGD Code: The "International Maritime Dangerous Goods Code" for the transport of dangerous goods by sea.

Level of risk: Magnitude of a risk or combination of risks, expressed in terms of the combination of consequences and their likelihood.

Likelihood: Chance of something happening.

Note 1 to entry: In risk management terminology, the word "likelihood" is used to refer to the chance of something happening, whether defined, measured or determined objectively or subjectively, qualitatively or quantitatively, and described using general terms or mathematically (such as a probability or a frequency over a given time period).

Note 2 to entry: The English term “likelihood” does not have a direct equivalent in some languages; instead, the equivalent of the term “probability” is often used. However, in English, “probability” is often narrowly interpreted as a mathematical term. Therefore, in risk management terminology, “likelihood” is used with the intent that it should have the same broad interpretation as the term “probability” has in many languages other than English.

Liquid:A substance or mixture which at 50^{o}C has a vapour pressure of not more than 300 kPa,which is not completely gaseous at 20^{o}C and at a standard pressure of 101.0 kPa,and which has a melting point initial melting point of 20^{o}C less at a standard pressure of 101.3 kPa.a viscous substance or mixture for which specific melting point cannot be determined shall be subjected to the ASTM 4359-90 tests;or to the test for determining fluidityprescribed in section 2.3.4 of the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).

LD50 is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals.

Local Effect: The failure effect as it applies to the item under analysis.

Major Accident: An occurrence such as a major emission, fire or explosion resulting from uncontrolled developments in the course of the operation of any establishment covered by this Directive, and leading to a serious danger to human health or the environment, immediate or delayed, inside or outside the establishment, and involving one or more dangerous substances.”

M-factor: A multiplying factor. It is applied to the concentration of a substance classified as hazardous to the aquatic environment acute category 1 or chronic category 1 and is used to derive by the summation method the classification of a mixture in which the substance is present.

Manufacturer: Any naturalor legal person established within the Union who manufactures a substance within the Union.

Mixture: A mixture or solution composed of two or more substances.

Monitoring: Continual checking, supervising, critically observing or determining the status in order to identify change from the performance level required or expected.

Note 1 to entry: Monitoring can be applied to a risk management framework, risk management process, risk or control.

Monomer: A substance which is capable of forming covalent bonds with a sequence of additional like or unlike molecules under the conditions of the relevant polymer-forming reaction used of the particular process.

Mutagen: An agent giving rise to an increased occurrence of mutations in populations of cells and /or organisms.

Mutation: A permanent change in the amount or structure of the genetic material in a cell.

Notifier: The manufacturer or the importer, or group of manufacturers or importers notifying to the Agency.

Next Higher Level Effect: The failure effect as it applies at the next higher indenture level.

Organic Peroxide: A liquid or solid organic substance which contains the bivalent –O-O structure and may be considered a derivative of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. The terms also include organic peroxide formulations.

OxidizingGas: Any gas which may, generally by providingoxygen, cause or contribute to the combustion of other material more than air does.

OxidizingLiquid: A solid which, while in itself not necessarily combustible, may generally by yielding oxygen, cause or contribute of other material.

OxidizingSolid: A solid which, while in itself not necessarily combustible, may generally by yielding oxygen, cause or contribute of other material.

Packaging: The container in which materials or goods are received or held for transport, including anything that enables the container to receive or hold the material or goods.

Packing: Containers or other items used to contain hazardous materials as per the appropriate packaging requirements.

Pictogram, Label, Symbol: Different types of warning sign.

Pollution: Residual discharges of emissions to the air or water following application of emission control devices.

Prevention of Pollution: The use of processes, practices, methods or products that avoid, reduce or control pollution. These may include recycling, treatment, process changes, control mechanisms, efficient use of resources and material substitution.

Probability: The likelihood of the failure occurring.

PyrotechnicSubstance: A substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of mondetonative self-sustaining exothermic chemical reactions.

REACH and REACH Regulation: Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals.

Recycling: The process of re-using material for the production of new goods or services on the same quality level. If the quality of the goods and services produced with recycled material is lower, then the process is known as down cycling.

Remarks / Mitigation / Actions: Additional info, including the proposed mitigation or actions used to lower a risk or justify a risk level or scenario.

Residual Risk: Risk remaining after risk treatment.

Note 1 to entry: Residual risk can contain unidentified risk.

Note 2 to entry: Residual risk can also be known as “retained risk”.

Resources: Materials found in the environment that can be extracted from the environment in an economic process. There are abiotic resources (non-renewable) and biotic resources (renewable).

Reuse: The additional use of a component, part, or product after it has been removed from a clearly defined service cycle. Reuse does not include reformation. However, cleaning, repair, or refurbishing may be done between uses.

Review: Activity undertaken to determine the suitability, adequacy and effectiveness of the subject matter to achieve established objectives.

Note 1 to entry: Review can be applied to a risk management framework, risk management process, risk or control.

Risk: Effect of uncertainty on objectives.

Note 1 to entry: An effect is a deviation from the expected — positive and/or negative.

Note 2 to entry: Objectives can have different aspects (such as financial, health and safety, and environmental goals) and can apply at different levels (such as strategic, organization-wide, project, product and process).

Note 3 to entry: Risk is often characterized by reference to potential events and consequences, or a combination of these.

Note 4 to entry: Risk is often expressed in terms of a combination of the consequences of an event (including changes in circumstances) and the associated likelihood of occurrence.

Note 5 to entry: Uncertainty is the state, even partial, of deficiency of information related to, understanding or knowledge of an event, its consequence, or likelihood.

Risk Analysis: Process to comprehend the nature of risk and to determine the level of risk.

Note 1 to entry: Risk analysis provides the basis for risk evaluation and decisions about risk treatment.

Note 2 to entry: Risk analysis includes risk estimation.

Risk Criteria: Terms of reference against which the significance of a risk is evaluated.

Note 1 to entry: Risk criteria are based on organizational objectives, and external and internal context.

Note 2 to entry: Risk criteria can be derived from standards, laws, policies and other requirements.

Risk Priority Number (RPN): Severity (of the event) * Probability (of the event occurring) * Detection (Probability that the event would not be detected before the user was aware of it).

Risk Assessment: A process to determine the relationship between the predicted exposure and adverse effects in four steps: hazard identification, dose-response assessment, exposure assessment and risk characterisation. See also 'targeted risk assessment'.

Risk Characterisation: Estimation of the incidence and severity of the adverse effects likely to occur in a human population or environmental compartment due to actual or predicted exposure to a substance.

Risk Evaluation: Process of comparing the results of risk analysis with risk criteria to determine whether the risk and/or its magnitude is acceptable or tolerable.

Note 1 to entry: Risk evaluation assists in the decision about risk treatment.

Risk Identification: Process of finding, recognizing and describing risks.

Note 1 to entry: Risk identification involves the identification of risk sources, events, their causes and their potential consequences.

Note 2 to entry: Risk identification can involve historical data, theoretical analysis, informed and expert opinions, and stakeholder's needs.

Risk Management: Coordinated activities to direct and control an organization with regard to risk.

Risk Management Framework: Set of components that provide the foundations and organizational arrangements for designing, implementing, monitoring, reviewing and continually improving risk management throughout the organization.

Risk Management Process: Systematic application of management policies, procedures and practices to the activities of communicating, consulting, establishing the context, and identifying, analysing, evaluating, treating, monitoring and reviewing risk.

Risk Source: Element which alone or in combination has the intrinsic potential to give rise to risk.

Note 1 to entry: A risk source can be tangible or intangible.

Risk treatment: Process to modify risk.

Note 1 to entry: Risk treatment can involve:

avoiding the risk by deciding not to start or continue with the activity that gives rise to the risk;

taking or increasing risk in order to pursue an opportunity;

removing the risk source;

changing the likelihood;

changing the consequences;

sharing the risk with another party or parties (including contracts and risk financing); and

retaining the risk by informed decision.

Note 2 to entry: Risk treatments that deal with negative consequences are sometimes referred to as “risk mitigation”, “risk elimination”, “risk prevention” and “risk reduction”.

Note 3 to entry: Risk treatment can create new risks or modify existing risks.

Safety Data Sheet (SDS): A document used for the manufacturing and importing of hazardous material. Safety Data Sheets specify the type of material and the properties associated with health and safety hazards.

Segregation: Means separation from other substances (including dangerous goods) so that a loss of containment cannot cause a serious incident.

Separation: Relation to the separation of dangerous goods from a person, property or thing, means the physical separation of the dangerous goods from the person, property or thing, by either distance or a physical barrier.

Severity: The consequences of a failure mode. Severity considers the worst potential consequence of a failure, determined by the degree of injury, property damage, system damage and/or time lost to repair the failure.

Signal Word: A Word that indicates the relative level of severity of hazards to alert the potential reader of the hazard; the following two levels are distinguished.

Skin Corrosion: The production of irreversible damage to the skin namely visible necrosis through the epidermis and into the dermis, following the application of a test substance up to 4 hours.

Skin Irritation: The production of reversible damage to the skin following the application of a test substance for up to 4 hours.

Solid Waste: Solid products or materials disposed of in landfills, incinerated or composted.

System: A collection of operations that perform a desired function.

Targeted risk assessment: A less extensive, more specifically focused evaluation (because of a specific concern) than a comprehensive risk assessment.

Tiered Approach: Proportionate effort in relation to the volumes, intrinsic properties, exposure and/or use of chemicals; see chapter 3 for further explanation.

UN number: It is four-digit numbers that identify hazardous substances, and articles in the framework of international transport.

Waste: An output with no marketable value that is discharged to the environment. Normally the term "waste" refers to solid or liquid materials.

Warming Means: a signal Word indicating the less severe hazard categories.

Waterborne Waste: Discharge to water of pollutants.

Worker: Person engaged by an occupier to work at the occupier's premises.

Workplace, Plant: Any place, whether or not in a building or structure, where persons work who are employed under a contract of employment or a contract of training or who are self-employed persons.

CHAPTER 1

1. RISK MANAGEMENT

1.1. Introduction

1.1.1. Objective of the course

The purpose of Risk Management course is to define and detect the main risk situations associated with major industrial accidents, and collect all necessary and suitable methodologies related to analysis and assess these risks.

In order to provide right background, the SEVESO Directive is the most important code to take into account. The SEVESO Directive aims to prevent major industrial accidents involving dangerous substances and limit the consequences to people and/or the environment.

1.1.2. Identification of the course

The recurrence of industrial accidents related to chemical plants has promoted the development in the last decades of some specific management systems, which share elements with systems currently more widespread such as those of quality management and occupational safety or the environmental. Recent studies show that simply effective action not only reduces occurrence of incidents and accidents but also allows to optimize the costs associated to the industrial activity.

1.1.3. Outcomes of the course

Over the last few decades, there has been an increase in public awareness at risk generated by industrial activities whether for people the environment especially those handling hazardous substances. This awareness has always gone hand in hand with the appearance of industrial accidents of high media coverage (Bhopal, Seveso, Toulouse, Buncefield, Deep Water Horizon...)

The industry responded to this increased public awareness by improving its facilities and safety procedures. Simultaneously the authorities have been creating a normative body with lessons learned from the past to prevent the recurrence of the major industrial accidents. At the same time, the dimensions and complexity of industrial establishments have increased and thus the investment costs, which means that the financial risk associated with a loss of production or damage to the installations has increased. It seems reasonable to consider that these trends will continue in the near future.

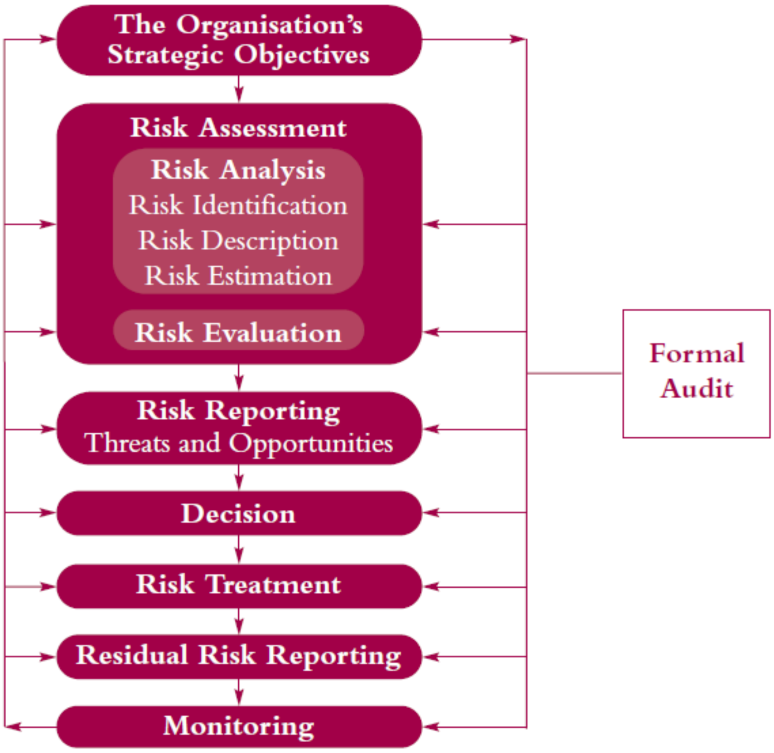
This course will focus the risk of major accidents with the potential to involve loss of human lives without leaving aside risks for installations and the environment (environment risk is addressed elsewhere in the course).

1.2. Risk management

Organizations of all types and sizes face internal and external factors and influences that make it uncertain whether and when they will achieve their objectives. The effect this uncertainty has on an organization's objectives is “risk”.

All activities of an organization involve risk. Organizations manage risk by identifying it, analysing it and then evaluating whether the risk should be modified by risk treatment in order to satisfy their risk criteria. Throughout this continuous and developing process (figure 1.1), they communicate and consult with stakeholders and monitor and review the risk and the controls that are modifying the risk in order to ensure that no further risk treatment is required. This course describes this systematic and logical process in detail.

Figure. 1.1. The process of risk management.



When implemented and maintained in accordance with this course, the management of risk enables an organization to, for example:

- increase the likelihood of achieving objectives;
- encourage proactive management;
- be aware of the need to identify and treat risk throughout the organization;
- improve the identification of opportunities and threats;
- comply with relevant legal and regulatory requirements and international norms;
- improve mandatory and voluntary reporting;
- improve governance;
- improve stakeholder confidence and trust;
- establish a reliable basis for decision making and planning;
- improve controls;
- effectively allocate and use resources for risk treatment;
- improve operational effectiveness and efficiency;
- enhance health and safety performance, as well as environmental protection;
- improve loss prevention and incident management;
- minimize losses;
- improve organizational learning; and
- improve organizational resilience.

In the field of Seveso directive, the risk management is supported in the obligation of the industries to have a Safety Management System (SMS) where the enterprises define how they manage the following matters in order to minimize the risk of having a major accident:

- organization and personnel;
- identification and evaluation of major hazards;
- operational control;
- management of change;
- planning for emergencies;
- monitoring performance;
- audit and review;

The next part of the course will focus on one part of this SMS that is the Identification and Evaluation of major hazards.

1.3. Risk assessment

According to ISO 31000, Risk Assessment is the “overall process of risk analysis and risk evaluation”. Risk assessment involves a series of steps as described below:

Step 1: Identification of the hazard, based upon consideration of factors such as the physical and chemical properties of the fluids being handled, the arrangement of equipment, operating and maintenance procedures and processing conditions. External hazards such as environmental conditions, neighbouring industries, etc. also need to be considered at this stage.

Step 2: Assessment of the risk arising from the hazards and consideration of its tolerability to personnel, the facility and the environment. This normally involves the identification of initiating events, identification of possible accident sequences, estimation of the probability of occurrence of accident sequences and assessment of the consequences. The acceptability of the estimated risk must then be judged based upon criteria appropriate to the particular situation.

Step 3: Elimination or reduction of the risk where this is deemed to be necessary. This involves identifying opportunities to reduce the probability and/or consequence of an accident.

1.3.1. Risk analysis

Risk analysis is the process to comprehend the nature of risk and to determine the level of risk. This process is divided into risk identification and risk estimation.

1.3.1.1. Risk identification

The level and extent of risk identification activities vary depending on the scale of the installation and the stage in the installation life cycle when the identification and assessment process is undertaken.

For example:

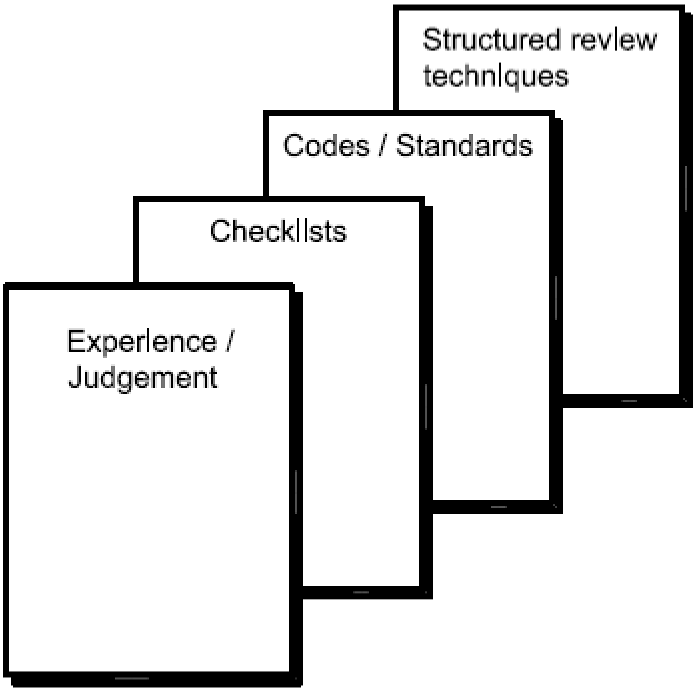
- complex installations, e.g. large production industries incorporating complex facilities, are likely to require detailed studies to address hazardous events such as fires, explosions, toxic releases, environmental impact, structural damage, etc.;

- for simpler installations, e.g. industries with limited process facilities, it may be possible to rely on application of recognized codes and standards as a suitable base which reflects industry experience for this type of facility;
- for installations which are a repeat of earlier designs, evaluations undertaken for the original design may be deemed sufficient to determine the measures needed to manage hazardous events;
- for installations in the early design phases, evaluations will necessarily be less detailed than those undertaken during later design phases, and will focus on design issues rather than management and procedural aspects. Any design criteria developed during these early stages need to be verified once the installation is operational.

Risk identification activities may need to be reviewed and updated if significant new issues are identified or if there is significant change to the installation.

Shows approaches with differing levels of complexity that may be used for risk identification.

Figure. 1.2. Approaches to hazards and risk assessment.



In many circumstances, the knowledge and expertise of experienced staff using a structured approach may be sufficient to manage risk.

Checklists are quick and easy to use, and can help determine whether design standards and practices are met and whether previously recognized hazards are properly addressed.

Where the experience gained by industry has been incorporated into codes and standards, a high level of safety can be achieved by checking for compliance with these standard practices in design, construction, operation and maintenance.

Structured review techniques can be used to identify and evaluate previously unforeseen hazards and unintended events that are not adequately addressed by the previous methods.

The aim of the course in this part is to show and describe some structured methodologies (see table 1.1.) to identify the risks, and to get more in deep in the HAZOP methodology.

Table.1.1. Structured methodologies for risk identification.

Structured Methodologies
1. Hazard Identification (HAZID) 2. Preliminary Hazard analysis (PHA) 3. Failure mode and effect analysis (FMEA) 4. Event Tree/Fault Tree Analysis (ET/FTA) 5. HAZOP Analysis

A. Hazard identification - HAZID

HAZID is a technique for the identification of all significant hazards associated with the particular activity under consideration.

The process normally adopted is to firstly identify all the possible undesirable consequences that could occur and then to identify hazards which, when realized, would cause that consequence. It is usual to include in the hazard list all reasonably foreseeable hazards, without deciding whether each hazard poses a significant risk to the activity in question. Once the gross list of hazards has been established, each hazard is then reviewed to see whether it is significant and should be evaluated further.

A structured approach to the identification of undesirable consequences is normally adopted starting with the broad categorizations such as human impacts, environmental impacts and economic impacts.

Each of these categories can then be further subdivided by the type of resulting damage, for example, toxic exposure, thermal exposure, overpressure, mechanical force, radiation, electrical shock, etc. The more precisely the consequences of interest are defined, the easier it will be later to identify hazards. Checklists, hazard registers from similar activities and previous HAZIDs are frequently used in order to assist in the task of consequence identification and hazard identification.

Once the consequences of interest have been defined, the analyst can identify those system, process and plant hazards which, when realized, give rise to the consequence. Common methods for hazard identification include analysing process material properties and process conditions, reviewing organization and industry experience, developing interaction matrices, and applying hazard evaluation techniques such as fault trees or coarse failure modes and effects analysis. It is important at this stage to think as widely as possible in order to ensure that no foreseeable hazards are overlooked.

Each hazard listed is assessed to determine whether it is relevant to the situations and activities being considered. At this stage no decisions are taken as to the importance or significance of the hazard, which is assessed later. All hazards identified as relevant are added to a gross list of hazards.

Once the gross list of hazards applicable to the particular situation has been prepared (either by the use of a hazard hierarchy or by consideration of consequences), each hazard is assessed to determine whether it insignificant or not. Typical reasons for classification of a hazard as not significant are as follows:

- very low frequency of occurrence, for example impact by a plane;
- insignificant effect on risk levels, for example release of gas from a pipeline a considerable distance from an installation;
- the effect of realization of a hazard may be included in another more severe hazard.

It is important to record both the gross list of hazards and the reasons for classifying some as not significant. This allows easy reassessment of the hazards list in the event of changing process or operational conditions. All the risk dimensions (personnel, environment and assets) need to be carefully considered before hazards are classified as non-significant.

It is also normal practice to prepare a formal hazards register, detailing each hazard together with appropriate data such as potential cause, potential consequence, system, equipment and geographical location (as appropriate) and some form of identification reference. Where possible, hazards are often grouped to assist in reducing further computational effort.

B. Preliminary hazards analysis (PHA)

PHA is an analytical technique used to identify hazards which, without adequate precautions, will give rise to a hazardous event. Typical hazardous event sources considered include oil and gas under high pressure, other fluids at high temperature, objects at height (lifted items), objects at velocity, explosives, radioactive materials, noise, inflammable materials, toxic materials, etc.

PHA is often used to evaluate hazards early in a project, being undertaken at the conceptual and front-end engineering stages. It does not require detailed design to be completed, but allows the identification of possible hazards at an early stage and thus assists in selection of the most advantageous arrangement of facilities and equipment.

The general process adopted involves the following steps:

- definition of the subsystems and operational modes;
- identification of the hazards associated with the particular subsystem or operation;
- definition of the particular hazardous event resulting from realization of the hazard;
- estimation of the probability of the event occurring and the possible consequence of each of the hazardous situations, and then using a particular set of rules to categorize the probabilities and consequences;
- identify and evaluate actions to be taken to reduce the probability of the hazardous event occurring or to limit the consequence;
- evaluate the interaction effect of different hazardous events and also consider the effects of common-mode and common-cause failures.

PHA is undertaken in a structured manner, usually using some form of table. Each hazardous event that has been identified for the particular subsystem or operation is studied in turn and recorded in one line of the table, arriving at a "risk rating" either for that particular hazardous event or the subsystem or operation.

PHA is often followed by more detailed FMEA and HAZOPs at a later stage of the design process.

C. FMEA failure mode and effect analysis and event/fault tree analysis

These methodologies are shown in more detailed in the course module "Accident Analysis".

D. Hazard and operability methodology (HAZOP)

In HAZOP analysis, an interdisciplinary team uses a systematic approach to identify hazards and operability problems occurring as a result of deviations from the intended range of process conditions. An experienced team leader systematically guides the team through the plant design, using a fixed set of "guide words" (Table 1.2) which are applied to specific "process parameters" (Table 1.3) at discrete locations or "study nodes" in the process system (figure1.3). The "study node" may be either a discrete point in the process system or it may be a particular run of piping.

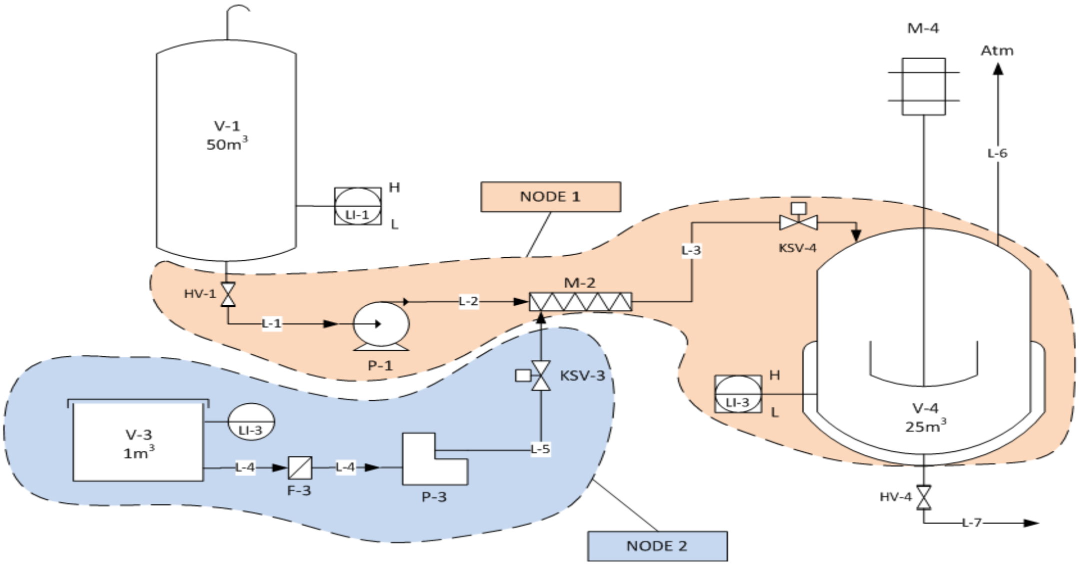
Table. 1.2. HAZOP guidewords.

Guideword	Meaning
NO (NOT/NONE)	*None* of the design intention is achieved
MORE (MORE OF)	*More* (quantitative increase) of a parameter
LESS (LESS OF)	*Less* (quantitative increase) of a parameter
AS WELL AS	An additional activity occurs *as well as* the design intention
PART OF	Only *part of* the design intention is achieved
REVERSE	The *reverse* (logical opposite) of the design intention occurs
OTHER THAN	Complete substitution-some activity other than the design intention takes places
Additional guidewords that are useful for studying procedures or batch operation are: **Before/after**: A step is attempted out of sequence, *before or after* it should occur. **Faster/slower**: Timing is incorrect and something happens *faster or slower* than intended	

Table.1.3. Example of parameters used in HAZOP.

HAZOP PARAMETERS	
FLOW	PHASE
PRESSURE	SPEED
TEMPERATURE	PARTICLE SIZE
MIXING	MEASURE
STIRRING	CONTROL
TRANSFER	pH
LEVEL	SEQUENCE
VISCOSITY	SIGNAL
REACTION	START/STOP
COMPOSITION	OPERATE
ADDITION	MAINTAIN
SEPARATION	SERVICES
TIME	COMMUNICATION

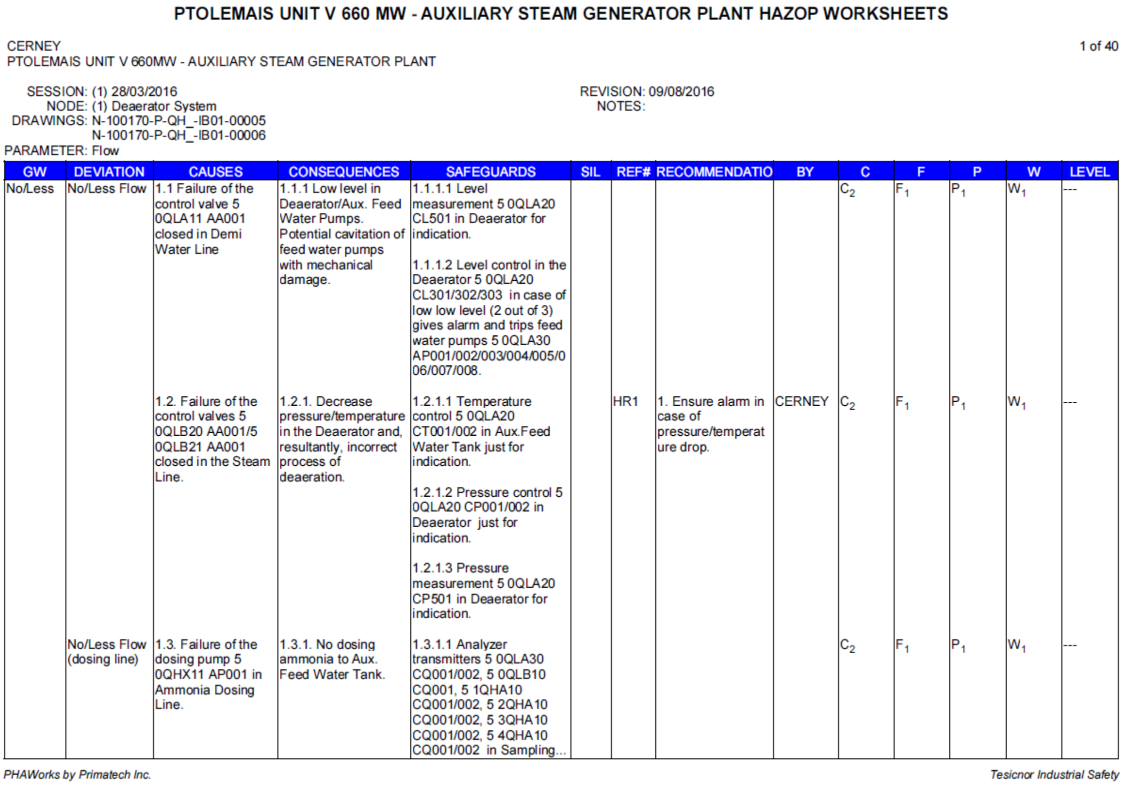
Figure.1.3. Example of PID. Process system divided in two nodes.



For example, the guide word "High" combined with the process parameter "level" results in questions concerning possible "high-level" deviations from the design intent. Sometimes, a leader will use checklists or process experience to help the team develop the necessary list of deviations that the team will consider in the HAZOP meetings. The team analyses the effects of any deviations at the point in question and determines possible causes for the deviation (e.g. operator error, blockage in outflow, etc.), the consequences of the deviations (e.g. spillage of liquid, pollution, etc.) and the safeguards in place to prevent the deviation (e.g. level control, piped overflow, etc.). If the causes and consequences are significant and the safeguards are inadequate, the details are recorded so that follow-up action can be taken. In some cases, the team can identify a deviation with a realistic cause but with indeterminable consequences, and in this event, follow-up studies to determine the possible consequences may be recommended.

The results from a HAZOP analysis are the team's findings, which include the hazards and operating problems identified, recommendations for changes in design, procedures, etc. to improve the system, and recommendations to conduct studies in areas where no conclusion was possible due to a lack of information. It is normal practice to record the results of the team discussions concerning the causes of deviations, their effects, and safeguards in place for each node or section of the process in a column-format table (figure 1.4).

Figure. 1.4. Example of HAZOP recording table.



PTOLEMAIS UNIT V 660 MW - AUXILIARY STEAM GENERATOR PLANT HAZOP WORKSHEETS

CERNEY
PTOLEMAIS UNIT V 660MW - AUXILIARY STEAM GENERATOR PLANT

1 of 40

SESSION: (1) 28/03/2016
NODE: (1) Deaerator System
DRAWINGS: N-100170-P-QH_-IB01-00005
N-100170-P-QH_-IB01-00006
PARAMETER: Flow

REVISION: 09/08/2016
NOTES:

GW	DEVIATION	CAUSES	CONSEQUENCES	SAFEGUARDS	SIL	REF#	RECOMMENDATIO	BY	C	F	P	W	LEVEL
No/Less	No/Less Flow	1.1 Failure of the control valve 5 0QLA11 AA001 closed in Demi Water Line	1.1.1 Low level in Deaerator/Aux. Feed Water Pumps. Potential cavitation of feed water pumps with mechanical damage.	1.1.1.1 Level measurement 5 0QLA20 CL501 in Deaerator for indication. 1.1.1.2 Level control in the Deaerator 5 0QLA20 CL301/302/303 in case of low low level (2 out of 3) gives alarm and trips feed water pumps 5 0QLA30 AP001/002/003/004/005/006/007/008.					C_2	F_1	P_1	W_1	---
		1.2. Failure of the control valves 5 0QLB20 AA001/5 0QLB21 AA001 closed in the Steam Line.	1.2.1. Decrease pressure/temperature in the Deaerator and, resultantly, incorrect process of deaeration.	1.2.1.1 Temperature control 5 0QLA20 CT001/002 in Aux.Feed Water Tank just for indication. 1.2.1.2 Pressure control 5 0QLA20 CP001/002 in Deaerator just for indication. 1.2.1.3 Pressure measurement 5 0QLA20 CP501 in Deaerator for indication.		HR1	1. Ensure alarm in case of pressure/temperature drop.	CERNEY	C_2	F_1	P_1	W_1	---
	No/Less Flow (dosing line)	1.3. Failure of the dosing pump 5 0QHX11 AP001 in Ammonia Dosing Line.	1.3.1. No dosing ammonia to Aux. Feed Water Tank.	1.3.1.1 Analyzer transmitters 5 0QLA30 CQ001/002, 5 0QLB10 CQ001, 5 1QHA10 CQ001/002, 5 2QHA10 CQ001/002, 5 3QHA10 CQ001/002, 5 4QHA10 CQ001/002 in Sampling...					C_2	F_1	P_1	W_1	---

PHAWorks by Primatech Inc.

Tesicnor Industrial Safety

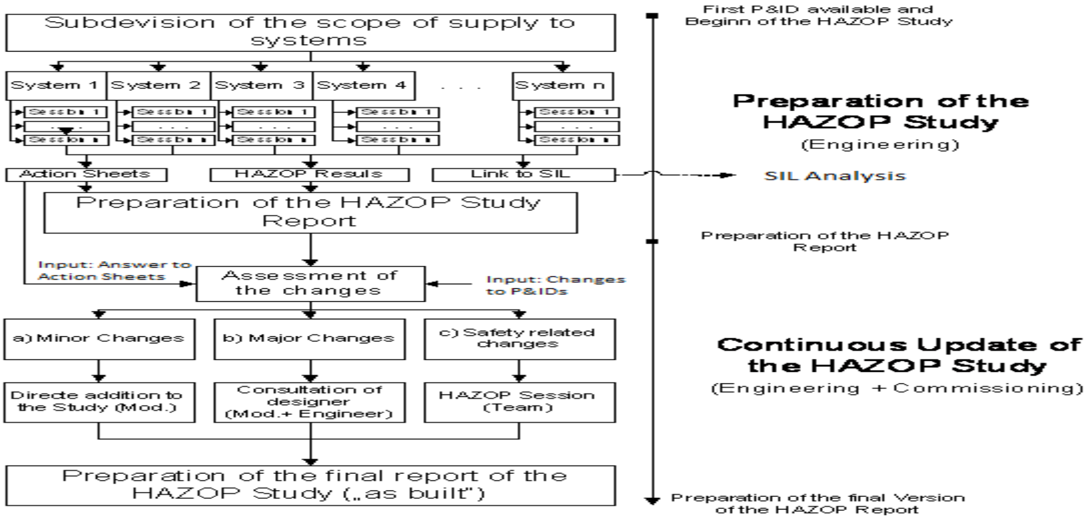
The objective of the HAZOP study is to identify possible problems areas and to make recommendations as to how the particular problems may be resolved. It is therefore critically important that clear procedures and responsibilities are established to ensure that the recommendations of the HAZOP analysis are reviewed and action taken by the appropriate personnel.

Access to detailed information concerning the design and operation of a process is necessary before a HAZOP analysis can be carried out, and thus it is most often used at the detailed design stage after the preparation of the P&IDs or during modification and operation of existing facilities. A HAZOP analysis also requires considerable knowledge of the process, instrumentation and operation either planned or actual, this information is usually provided by team members who are experts in these areas. Trained and experienced leaders are an essential part of an efficient, high-quality HAZOP analysis.

Typically, a HAZOP team consists of five to seven people with different backgrounds and experience in such aspects as engineering, operations, maintenance, health, safety and environment and so forth. It is normal for the team member who leads the analysis to be assisted by another, often referred to as the secretary, who records the results of the team's deliberations as the work proceeds. For a simple process or in a limited-scope review, a team can have as few as three or four people if they have the necessary skills and breadth of experience.

The figure.1.5. show the original steps to preparation and development for the team members.

Figure. 1.5. Steps to preparation and development of a HAZOP study.



1.3.2. Risk estimation

Once the hazards have been identified, the risks they present to personnel, environment and the facilities are evaluated.

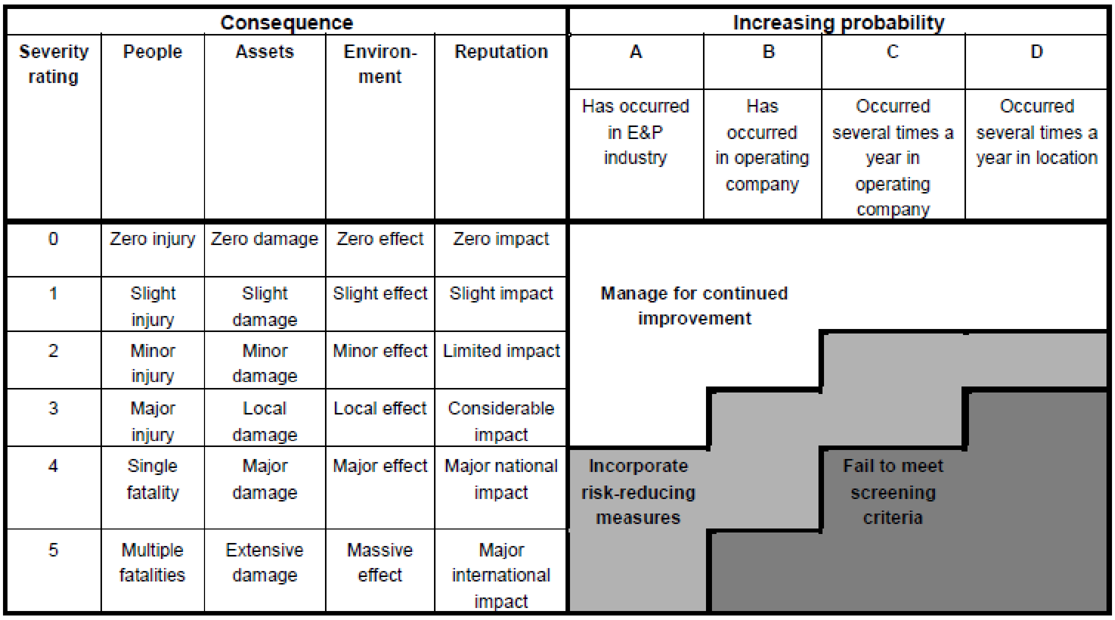
In evaluating risk, due consideration is given to both the likelihood (or frequency) of occurrence and the severity of consequences arising from the initiating hazardous event.

Risk in a specific location = Accident frequency x Damage

Risk estimation can be quantitative, semi quantitative or qualitative in terms of the probability of occurrence and the possible consequence.

In the qualitative or semi quantitative estimation, the different organizations or activities will find that different measures of consequence and probability will suit their needs best (Figure 1.6).

Figure. 1.6. Proposed risk matrix and consequences for the offshore industries.

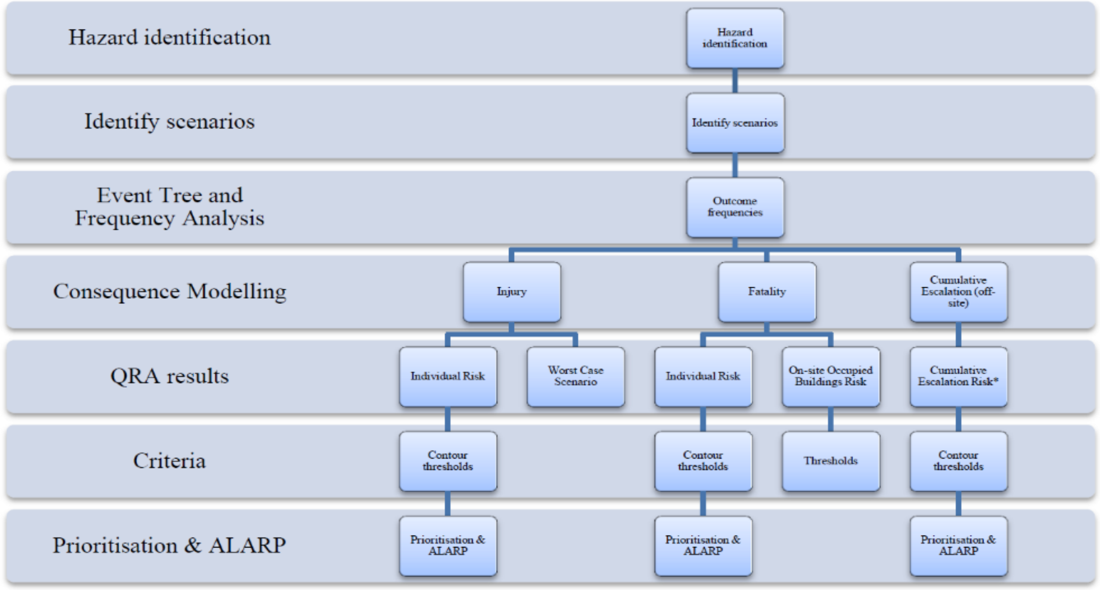


Consequence					Increasing probability			
Severity rating	People	Assets	Environ-ment	Reputation	A	B	C	D
					Has occurred in E&P industry	Has occurred in operating company	Occurred several times a year in operating company	Occurred several times a year in location
0	Zero injury	Zero damage	Zero effect	Zero impact				
1	Slight injury	Slight damage	Slight effect	Slight impact	**Manage for continued improvement**			
2	Minor injury	Minor damage	Minor effect	Limited impact				
3	Major injury	Local damage	Local effect	Considerable impact				
4	Single fatality	Major damage	Major effect	Major national impact	**Incorporate risk-reducing measures**		**Fail to meet screening criteria**	
5	Multiple fatalities	Extensive damage	Massive effect	Major international impact				

The quantitative estimation is done when international or national regulations (or corporative regulations) are compulsory or when assessing a qualitative o semi quantitative methodology, the risk estimated is over the screening criteria. In this cases a Quantitative Risk Assessment (QRA) is needed.

A QRA study is made up of a number of steps (Figure 1.7).

Figure 1.7. QRA study process.



*Cumulative Escalation Risk is modelled the same way as Individual Risk. The term 'Cumulative Escalation Risk' refers to the IR equivalent for structures, and is used to differentiate between risk to structures and risk to humans (IR)

The process starts with risk identification from which the scenarios to take forward in the QRA study are derived.

Outcome frequencies for these scenarios are then calculated using failure rates, event trees and modifiers.

Consequences are calculated to determine distances and footprints to specified harm levels grouped into specific categories:

- injury to people;
- fatality to people (both on-site and off-site);
- escalation off-site.

The required results are then presented. These are either in terms of consequence or risk:

- For consequence-based results, distances to specific harm levels and outcome frequencies should be provided and specified harm zones produced.
- For risk-based results, the groups of footprints to specified harm levels along with outcome frequencies and weather data for the different categories noted above are used to calculate individual risk. Individual risk is the summation of risks from all the scenarios within the defined Boundary and is usually calculated on a grid and presented graphically in the form of Iso-contours for specific risk levels. In addition, an occupied buildings assessment should be carried out.

These results are then compared to specified criteria. The criteria relate to different types of sensitive receptors, boundaries and land types.

The results of the risk evaluation are then prioritized to identify a set of scenarios for consideration for risk reduction to reduce the risk to ALARP. They also form a key input to emergency response planning.

1.3.2.1. Scenario list

See 1.3.1.1 of the present course. From the risk identification, a scenario list should be generated.

A scenario describes the conditions that might lead to a major accident and the potential consequences, which in most cases is the loss of containment (LOC) also known as the critical event (CE), of a hazardous substance, or the change of state of a solid substance, combined with particular conditions that eventually lead to a dangerous phenomenon as fire, explosion, and/or toxic release.

Here there are some examples of what are considered CE:

- Catastrophic failure and a range of hole sizes, and time of the release:
  - ✓ Instantaneous release of entire content (storage tanks)
  - ✓ Release of entire contents in 10 min. in a continuous and constant stream (storage tanks).
  - ✓ Continuous release of contents from a hole with an effective diameter of 10 mm (storage tanks).
  - ✓ Rupture (pipeline).
  - ✓ Leak with an effective diameter of 10% of the nominal diameter, up to a maximum of 50mm (pipeline).
  - ✓ Rupture of 10 pipes at same time (Heat exchangers and condensers).
  - ✓ Outflow at the maximum outflow rate (pressure relief valve).
  - ✓ Rupture of loading/unloading arm or hose (loading activities)
  - ✓ …
- Mischarging into reactors and storage tanks causing runaway reaction (particularly if causing release of toxic gas due to the reaction);
  - ✓ The main event to be modelled for a chemical reactor is catastrophic failure due to overpressure caused by runaway reaction. A worst case

substance released, between normal reactor contents and products should also be considered.

- ✓ If the site has storage tanks containing chemicals that would react to give a toxic gas, then the runaway reaction due to filling into the wrong tank should be considered. Consequences based on dispersion of toxic gas should be based on filling rate reacting until detection and shut down.

- Overfilling of storage tanks giving rise to explosion such as at Buncefield UK in 2005 (potential, unless eliminated by design, for VCE under conditions not previously expected to cause VCE).

1.3.2.2. Identification of dangerous phenomenon associated to the critical event and its physical effects

For each of the CE the different outcomes should be identified depending on the hazardous material. The range of potential outcomes considered should include (depending on the physical properties of the hazardous materials concerned):

- Pool fire: It applies to a stationary diffusion flame combustion of a liquid in an open enclosure with given dimensions.

Figure. 1.8. Pool fire.

The physical effects associated will be the thermal radiation and the direct flame contact.

- Jet fire: Ignition of a continuous leakage of flammable gases or vapours contained in pipes or containers with overpressure.

Figure. 1.9. Jet fire.

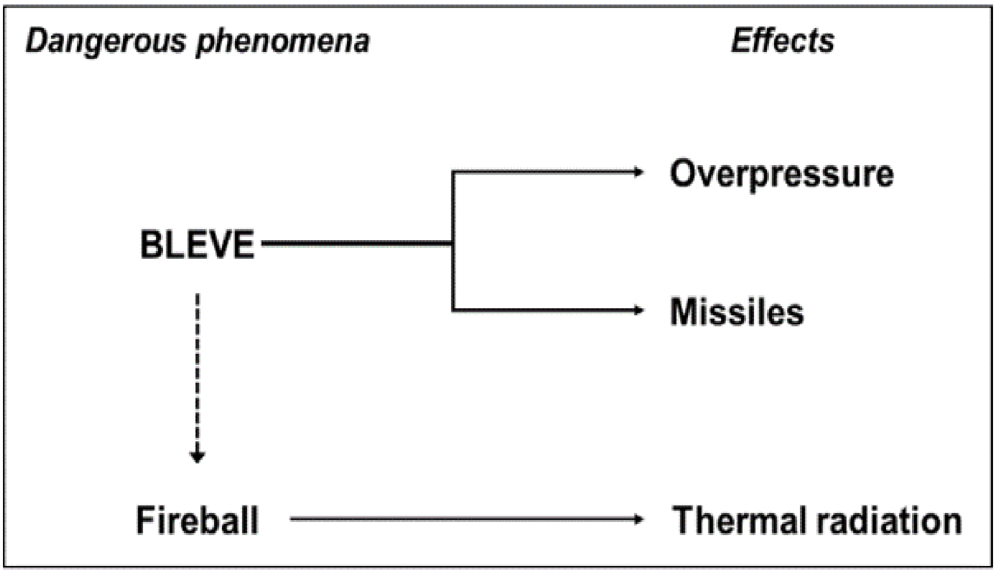
The physical effects associated will be the thermal radiation and the direct flame contact.

- BLEVE and Fireball: Boling Liquid Expanding Vapour Explosion. It represents catastrophic failure of a container storing a liquefied gas above boiling point at atmospheric pressure, and causing an immediate massive, liquid leakage into the atmosphere.

Figure. 1.10. Ball fire associated to a BLEVE.

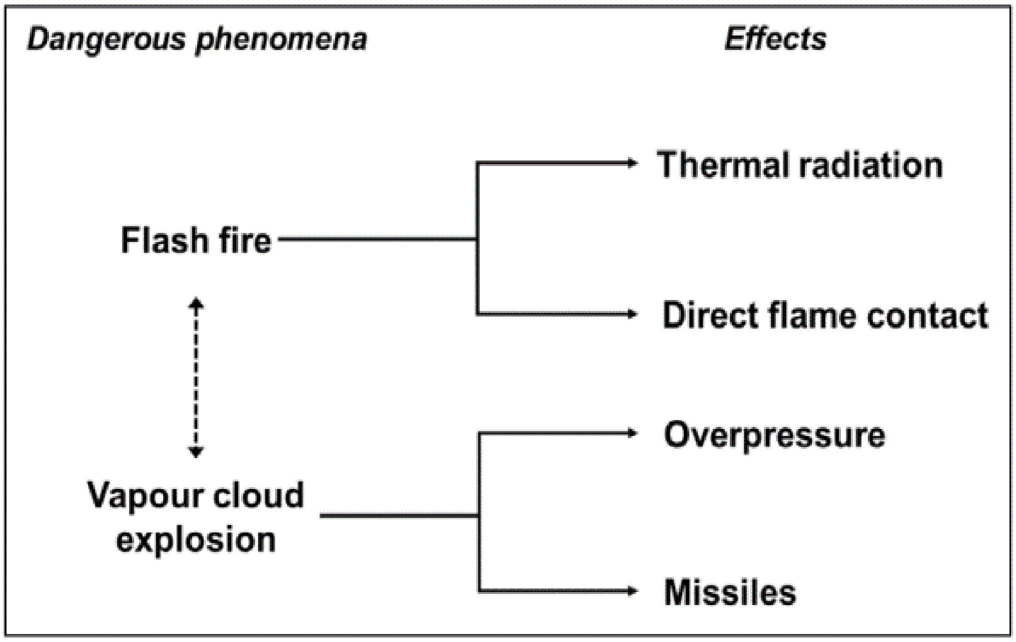
The physical effects are shown in figure 1.11.

Figure. 1.11. Physical effects of a fireball and BLEVE.



- Vapour cloud explosion (VCE) and Flash fire: The explosive blast of a cloud of flammable gas (with concentrations within the explosion limits) which is in an open or confined space, the pressure wave reaches a maximum pressure of about 1 bar in the ignition. Flash Fire is the progressive flame diffusion or premixed with low flame speed. No pressure wave is produced. The physical effects are shown in figure 1.12.

Figure. 1.12. Ball fire associated to a BLEVE.



- Pressure vessel burst e.g. due to runaway reaction or internal explosion;

Figure.1.13. Pressure vessel burst due to a pneumatic pressure test with air.

- Toxic release: plume dispersion of a toxic chemical

Figure. 1.14. Toxic release.

The occurrence of these phenomena depends on the substance, the conditions and the CE. The most representative event trees for the different CE (depending on the state of the substance) are given in the next figures.

Figure. 1.15. Event tree for an instantaneous release of a flammable gas.

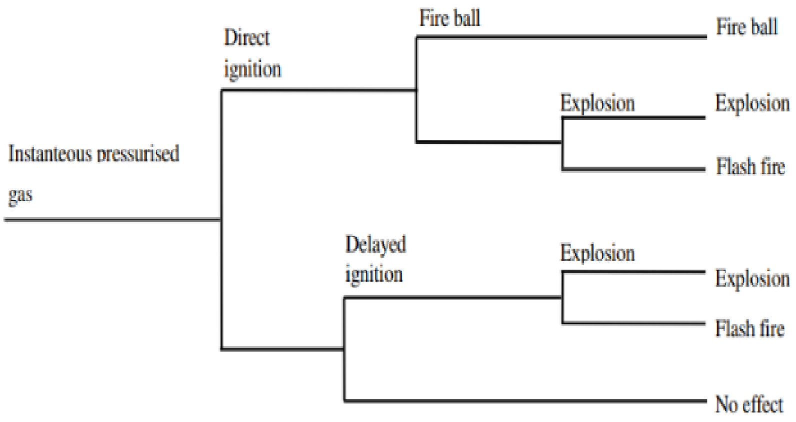


Figure. 1.16. Event tree for a continuous release of a flammable gas.

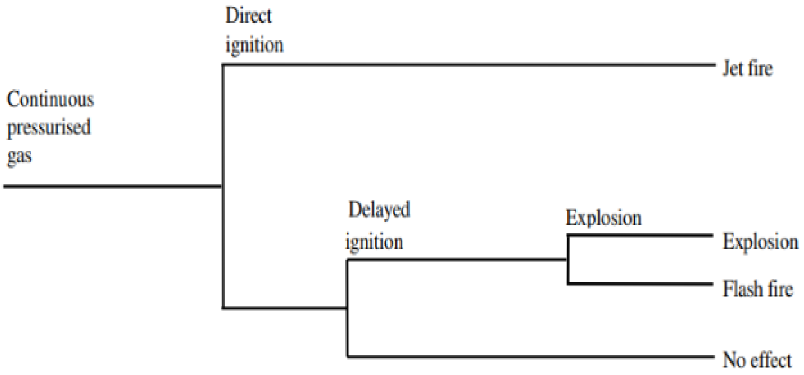


Figure. 1.17. Event tree for an instantaneous release of a pressurized liquefied flammable gas.

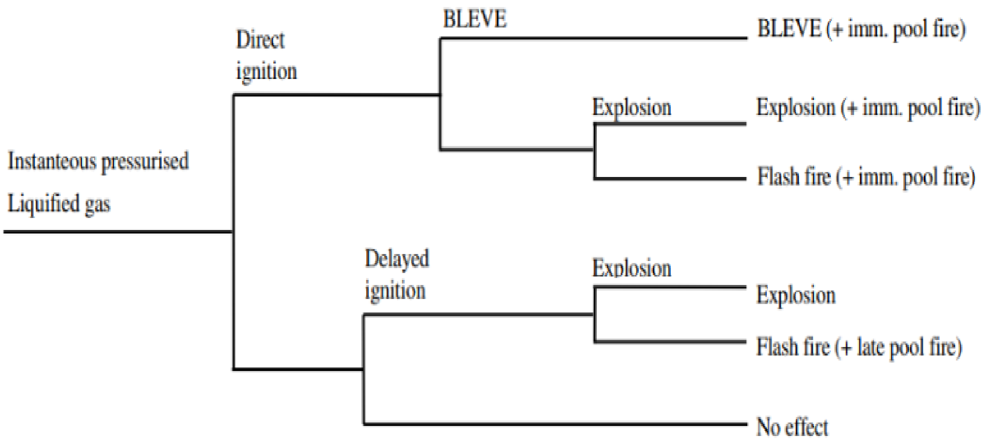


Figure. 1.18. Event tree for a continuous release of a pressurized liquefied flammable gas.

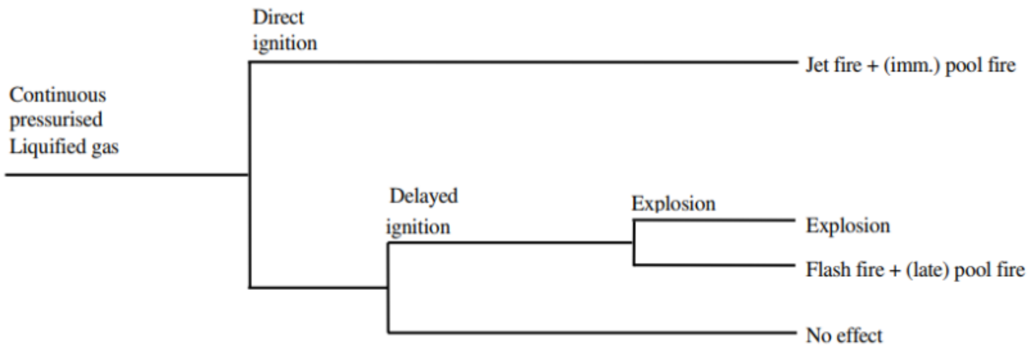
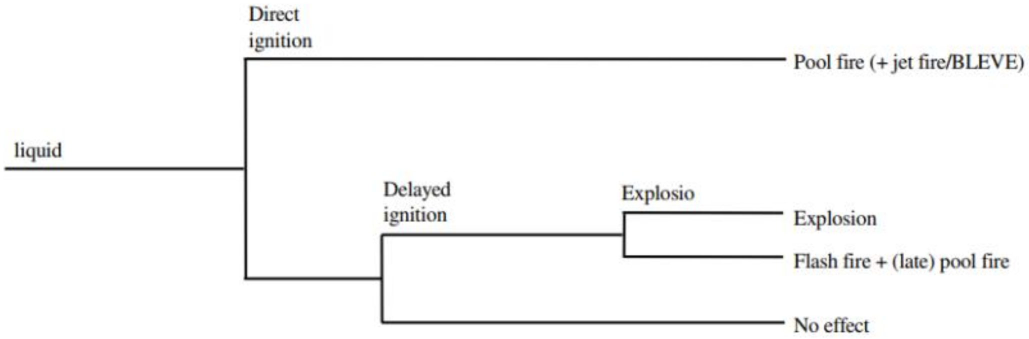


Figure. 1.19. Event tree for a release of a flammable liquid.



1.3.2.3. Frequency of the critical events and associated phenomenon

The likelihood of each event should be calculated. Frequency data for the critical event and the phenomenon associated should be obtained from an appropriate data source. For example:

- UK failure rates: (http://www.hse.gov.uk/landuseplanning/failure-rates.pdf) ;
- Reference manual Bevi Risk Assessments http://infonorma.gencat.cat/pdf/AG_AQR_2_Bevi_V3_2_01-07-2009.pdf
- Evaluation of the Dutch QRA directives for storage and transportation of flammable liquids - http://rivm.openrepository.com/rivm/handle/10029/262220
- Handbook of scenarios for assessing major chemical accident risks - http://publications.jrc.ec.europa.eu/repository/bitstream/JRC106029/jrc106029_online.pdf
- HSE UK RR1035- pipelines - http://www.hse.gov.uk/research/rrpdf/rr1035.pdf

- Institute of gas engineers and mangers (IGEM) – Pressure natural gas pipelines - http://www.igem.org.uk/media/220015/igem-td-2%20draft%20for%20comment%20(igem-tsp-12-156).pdf

1.3.2.4. Frequency modifiers

With suitable justification, it is acceptable to take credit for suitably designed hardware measures which reduce the frequency of the CE, for example:

- The design of a pipeline with higher wall thickness and reduced design stress (reduced ratio of operating pressure to design pressure) since these factors can reduce the frequency of failure as a result of third party activity (e.g. inadvertent impact of a buried pipeline with a mechanical excavator).
- Safety distances (for example, design of safety distances without a potential ignition source).
- Bunds.
- Blocking systems
- Excess flow valves.
- Non return valves.
- Detection and shutdown systems.
- Immobilizers and break away couplings.
- …

It may also be allowable to take credit for scenario-specific measures that incorporate operator action, e.g. to cool down a reactor or to stop filling for an overfilled vessel. Probability of failure needs to consider the availability of an operator (including, if action provides mitigation, that the operator might become a casualty) and the probability of human error.

‘Management factors’, unless strongly justified shall not be applied to historical failure frequencies of containment systems. Such measures may not be taken into account in modifying historical failure rates because some of the inventory of equipment items used to derive the historical failure rates will have had the risk reduction measure. Double-counting of the effects of a risk reduction measure is not allowed. For novel hardware risk reduction measures, credit might be allowable with suitable justification. Also, any credit given for an operator’s current excellent record of safety management, would need to be maintained over the life-time of the installation and cannot therefore be justified for QRA at the pre-construction stage (e.g. due to possible future changed ownership).

It is also acceptable to take credit for risk reduction measures which are part of the event tree following loss of containment (see Section 4.2 below). Credit may also be taken for hardware risk reduction measures, such as suitably designed passive fire protection in preventing escalation events, active fire protection systems, blast or fire walls, toxic refuge, specially designed control room, scrubbers, water deluxe, ...

This modifiers act as reducers of the frequency of the CE or minimize the frequency a phenomenon happens. Again, some modifiers have a probability of malfunction (for example in the case of automatic blocking system, the probability of failure per operation is equal to 0.001 and the time required for the closing of the blocking valves is equal to 2 minutes) and some has an effectiveness percentage (for example in the case of fire repression systems). The frequency databases are listed in 3.1.2.3.

Another way to justify the failure rate or the probability of failure on demand (PFD) of the systems is to justify with suitable IEC61508/ 61511 safety integrity level (SIL) for entire system including detection, logic, field wiring or equivalent, actuators and valves (table 1.4).

Table. 1.4. Safety integrity level and probability of failure on demand for low demand mode of operation.

Safety Integrity Level (SIL)	PFD Range
SIL4	$10^{-5} - 10^{-4}$
SIL3	$10^{-4} - 10^{-3}$
SIL2	$10^{-3} - 10^{-2}$
SIL1	$10^{-2} - 10^{-1}$
Not designed to achieve SIL	$< 10^{-1}$

1.3.2.5. Consequence modelling of dangerous phenomenon

After calculating the frequency of a CE and the dangerous events associated (accident frequency) it is the turn to calculate the damage done by the dangerous phenomenon. This is done by doing a consequence modelling.

Physical-chemical variables are set for each of the dangerous phenomenon, whose magnitude can be considered sufficiently representative to assess the extent of chemical, mechanical and thermal phenomena triggered after the accident. Areas affected by potential accidents are determined based on the distance to certain physical and chemical variables representative of dangerous phenomena reach a certain threshold values.

In ***dangerous chemical phenomena***, representative injury after the release of toxic clouds are forming toxic concentration or toxic dose defined.

$$D = C_{\max}^{n} \cdot t_{\exp}$$

Where:

D : Dosis

C_{max} **:** Maximum concentration of the substance in the air

t_{exp} : Exposure time in seconds

n **:** Substance exponent

The indices of maximum concentration of the substance in the air which are used, are the AEGL (Acute Exposure Guideline Levels). Originally proposed by the Environmental Protection Agency of the United States, defined three levels of damage (1, 2, 3), considering for each level reference periods: 30 minutes, 1, 4, and 8 hours, and in some cases also established for a period of 10 minutes. If the substance has not defined the previous index, GPRS (Emergency Response Planning Guidelines) published by the American Industrial Hygiene Association and/or TEEL (Temporary Emergency Exposure Limits) developed by the Department of Energy of the United States will be used. The latter two indices are set to the same levels of damage than those established for AEGL but in each case, for a single period: 1 hour to the GPRS and 15 minutes to the TEEL. For more than 15 minutes at rates TEEL times, it is determined by extrapolating the Haber Law:

$$C_{\max} = TEEL \cdot \frac{15}{t_p}$$

Hazardous thermal-type phenomenonis caused by rapid oxidation of combustible substances but not explosive. The flame produced can be stationary or progressive, and in both cases the mechanism of heat transfer by radiation is performed. The radiation dose received by humans is used to evaluate these phenomena and is expressed as follows:

$$D = I_m^{\frac{4}{3}} \cdot t_{\exp}$$

where:

I_m : average intensity received, in kW/m

t_{exp} : exposure time, in seconds.

This expression is valid for intensities higher than 1.7 kW/m^2, for lower values, the exposure time is irrelevant (population may be exposed for extended periods of time, since the flow of radiation can be dissipated the same speed as received).

In other cases, I > 1.7 kW/m^2, the exposure time is considered the time until reaching the affected area protected against radiation, where radiation is less than 1.7 kW/m^2.

The model population response usually adopted is the one in which a first reaction period of 5s where the population remains static and then escape occurs, away from the fire, at a speed of 4 m/s.

In ***dangerous mechanical phenomena*** (pressure waves and projectiles after explosions) the variables are local static pressure of the pressure wave pulse and integrated local value.

Once known the physical - chemical variables representative for the evaluation of the scope of the dangerous phenomenon, one is in a position to assess the consequences of such accidents. The models and software used and the basis for their selection for each specific outcome, considering applicability, should be stated clearly including version number. Where it is industry standard software with validated models, stating the inputs used and the models selected is sufficient. Otherwise, details of the calculations should be provided and justified accordingly. Industry standard software includes DNV PHAST; TNO Effects; CERC ADMS (particularly buoyant dispersion); Shell Global Solutions FRED; BP CIRRUS; SAFER TRACE. Note that standard software has had some validation and verification but this does not mean that uncertainty can be ignored. Also all software and models have limits of applicability which shall take into account.

1.3.2.6. Vulnerability modelling and criteria

The analysis of vulnerability due to hazardous phenomena associated with major accidents is done by applying the "Probit methodology."

This methodology involves the application of statistical correlations to estimate the adverse consequences on the population and other vulnerable elements (facilities and environment) of hazardous physical phenomena resulting from accidents.

The vulnerability of people is expressed as the number of individuals who, predictably, may be affected with some level of damage because of an accident. Moreover, the vulnerability of facilities can be quantified using economic indicators.

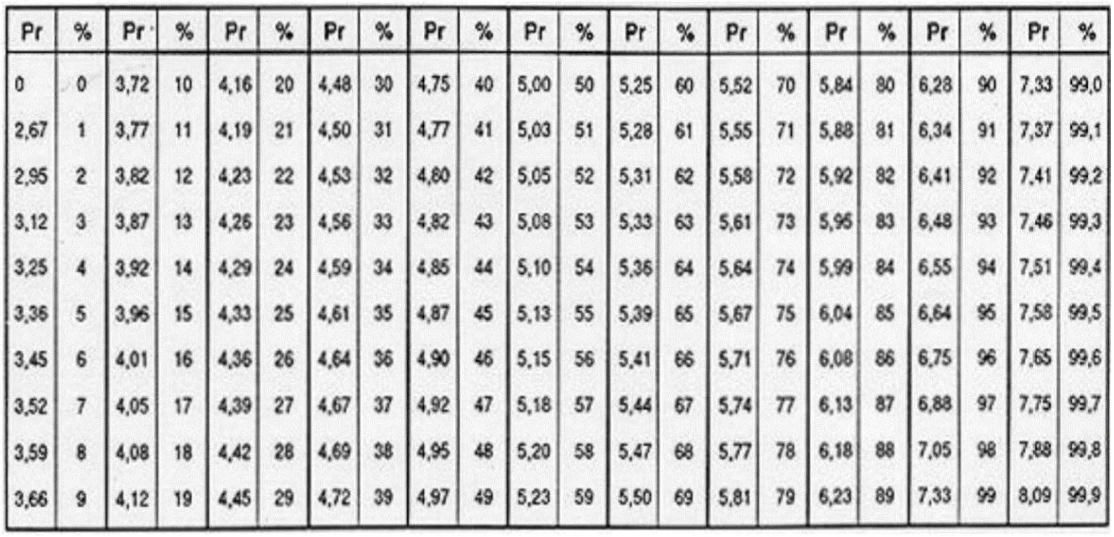
The response of a population to a hazardous physical phenomenon is distributed according to a log-normal law. The model is applicable only for those phenomena that are available "probit equation".

In these methodology calculates the variable Pr probit that depends on a number of parameters (constants k1 and k2, variable physical representative of accident, Z). These will have a value or another depending on the nature of the consequence being studied.

$$\mathrm{Pr} = k_1 + k_2 \cdot \ln(z)$$

Where Probit value (Pr) is tabulated as an equivalence or percentage of population affected (figure 1.20).

Figure. 1.20. Equivalence between values "Probit" and percentage of population affected.



Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%
0	0	3,72	10	4,16	20	4,48	30	4,75	40	5,00	50	5,25	60	5,52	70	5,84	80	6,28	90	7,33	99,0
2,67	1	3,77	11	4,19	21	4,50	31	4,77	41	5,03	51	5,28	61	5,55	71	5,88	81	6,34	91	7,37	99,1
2,95	2	3,82	12	4,23	22	4,53	32	4,80	42	5,05	52	5,31	62	5,58	72	5,92	82	6,41	92	7,41	99,2
3,12	3	3,87	13	4,26	23	4,56	33	4,82	43	5,08	53	5,33	63	5,61	73	5,95	83	6,48	93	7,46	99,3
3,25	4	3,92	14	4,29	24	4,59	34	4,85	44	5,10	54	5,36	64	5,64	74	5,99	84	6,55	94	7,51	99,4
3,36	5	3,96	15	4,33	25	4,61	35	4,87	45	5,13	55	5,39	65	5,67	75	6,04	85	6,64	95	7,58	99,5
3,45	6	4,01	16	4,36	26	4,64	36	4,90	46	5,15	56	5,41	66	5,71	76	6,08	86	6,75	96	7,65	99,6
3,52	7	4,05	17	4,39	27	4,67	37	4,92	47	5,18	57	5,44	67	5,74	77	6,13	87	6,88	97	7,75	99,7
3,59	8	4,08	18	4,42	28	4,69	38	4,95	48	5,20	58	5,47	68	5,77	78	6,18	88	7,05	98	7,88	99,8
3,66	9	4,12	19	4,45	29	4,72	39	4,97	49	5,23	59	5,50	69	5,81	79	6,23	89	7,33	99	8,09	99,9

Suitable and justified probit equations shall be used (e.g. those in the TNO Green Book or BEVI) for each dangerous phenomenon, for example:

For toxic substances

The probit for exposure to toxic substances is indicated using the relationship:

$$\Pr = a + b \cdot \ln(C^n \cdot dt)$$

where

Pr probit associated with the probability of dying

a, b, n constants for the toxicity of a substance

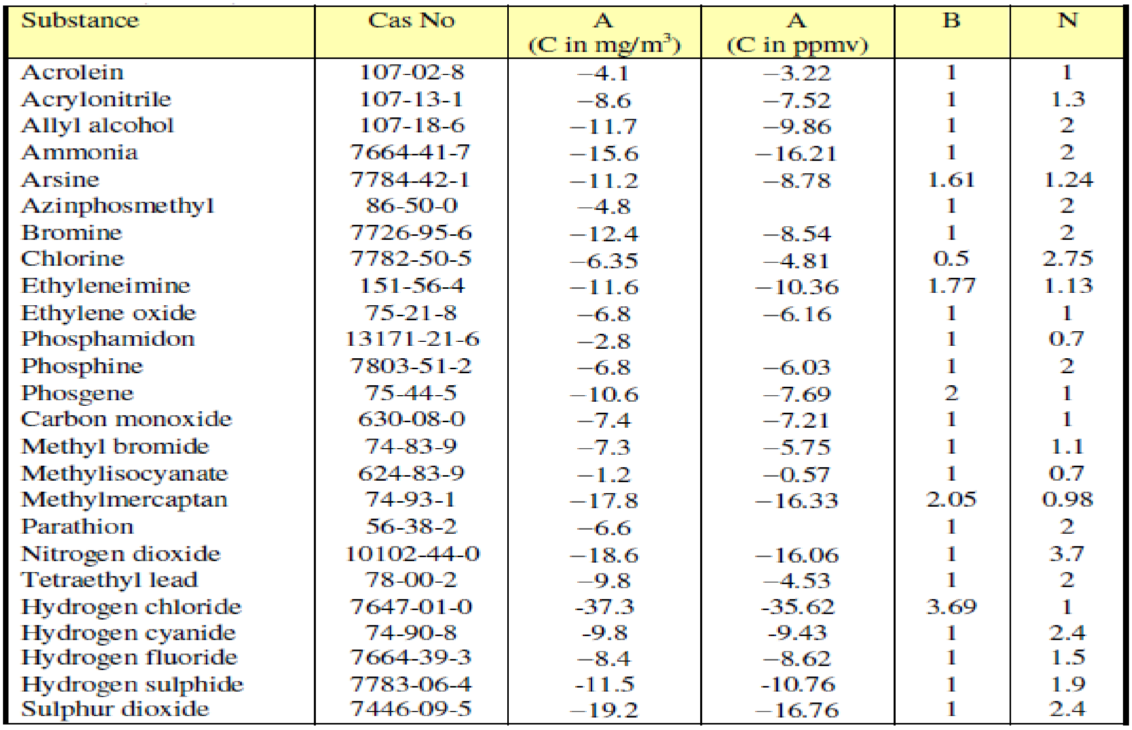
C concentration at time t (mg/m^3)

t exposure time (minutes)

The method to derive a probit relation, the evaluation procedure and the substances in procedure are described at the website of RIVM - http://www.rivm.nl/dsresource?objectid=2a89ce13-5e62-4597-9058-9fb38697e4d5&type=org&disposition=inline

Probit relationships have been determined for a number of substances. These are set out in Table 1.5.

Table. 1.5. Constants for the toxicity of a substance, a, b and n for the probit equation.



Substance	Cas No	A (C in mg/m^3)	A (C in ppmv)	B	N
Acrolein	107-02-8	–4.1	–3.22	1	1
Acrylonitrile	107-13-1	–8.6	–7.52	1	1.3
Allyl alcohol	107-18-6	–11.7	–9.86	1	2
Ammonia	7664-41-7	–15.6	–16.21	1	2
Arsine	7784-42-1	–11.2	–8.78	1.61	1.24
Azinphosmethyl	86-50-0	–4.8		1	2
Bromine	7726-95-6	–12.4	–8.54	1	2
Chlorine	7782-50-5	–6.35	–4.81	0.5	2.75
Ethyleneimine	151-56-4	–11.6	–10.36	1.77	1.13
Ethylene oxide	75-21-8	–6.8	–6.16	1	1
Phosphamidon	13171-21-6	–2.8		1	0.7
Phosphine	7803-51-2	–6.8	–6.03	1	2
Phosgene	75-44-5	–10.6	–7.69	2	1
Carbon monoxide	630-08-0	–7.4	–7.21	1	1
Methyl bromide	74-83-9	–7.3	–5.75	1	1.1
Methylisocyanate	624-83-9	–1.2	–0.57	1	0.7
Methylmercaptan	74-93-1	–17.8	–16.33	2.05	0.98
Parathion	56-38-2	–6.6		1	2
Nitrogen dioxide	10102-44-0	–18.6	–16.06	1	3.7
Tetraethyl lead	78-00-2	–9.8	–4.53	1	2
Hydrogen chloride	7647-01-0	-37.3	-35.62	3.69	1
Hydrogen cyanide	74-90-8	-9.8	-9.43	1	2.4
Hydrogen fluoride	7664-39-3	–8.4	–8.62	1	1.5
Hydrogen sulphide	7783-06-4	-11.5	-10.76	1	1.9
Sulphur dioxide	7446-09-5	–19.2	–16.76	1	2.4

The toxic vulnerability criteria is to find the areas of space given by the probability of occurrence of death giving the probability of 99%, 50% and 1%.

Flammable substances - heat radiation

The probability of dying, P lethal, of exposure to heat radiation (pool fire, flaring, fire ball) is given by the probit relationship:

$$\Pr = 36.28 + 2.56 \cdot \ln(I^{4/3} \cdot dt)$$

where

Pr probit associated with the probability of dying

I heat radiation at time t (W/m^2)

t exposure time (s)

The heat radiation vulnerability criteria is to find the areas of space given by the probability of occurrence of fatal burns, occurred due to the scene of fire giving the probability of death of 99%, 50% and 1%.

Overpressure – death from pulmonary hemorrhage (wave peak)

The probability of dying, P lethal, of exposure to overpressure is given by the probit relationship:

$$\Pr = 77.1 + 6.91 \cdot \ln(P)$$

Where:

Pr: Probit equation value

P: Maximum overpressure N/m^2

The overpressure vulnerability criteria is to find the areas of space given by the probability of occurrence of deaths from impact (metal fragments) or lung injury, due to explosion scenario occurred, giving the probability of death of 99%, 50% and 1%.

1.3.2.7. Outcomes of risk estimation: Individual and societal risk

The final objective of the Quantitative Risk Assessment (QRA) is to determine the value of the risk caused by an accident as a function of the product of the probability of occurrence for damage associated with it, expressing that risk in this type of study in terms of human fatalities.

Risk = Probability x Damage

A. Individual risk

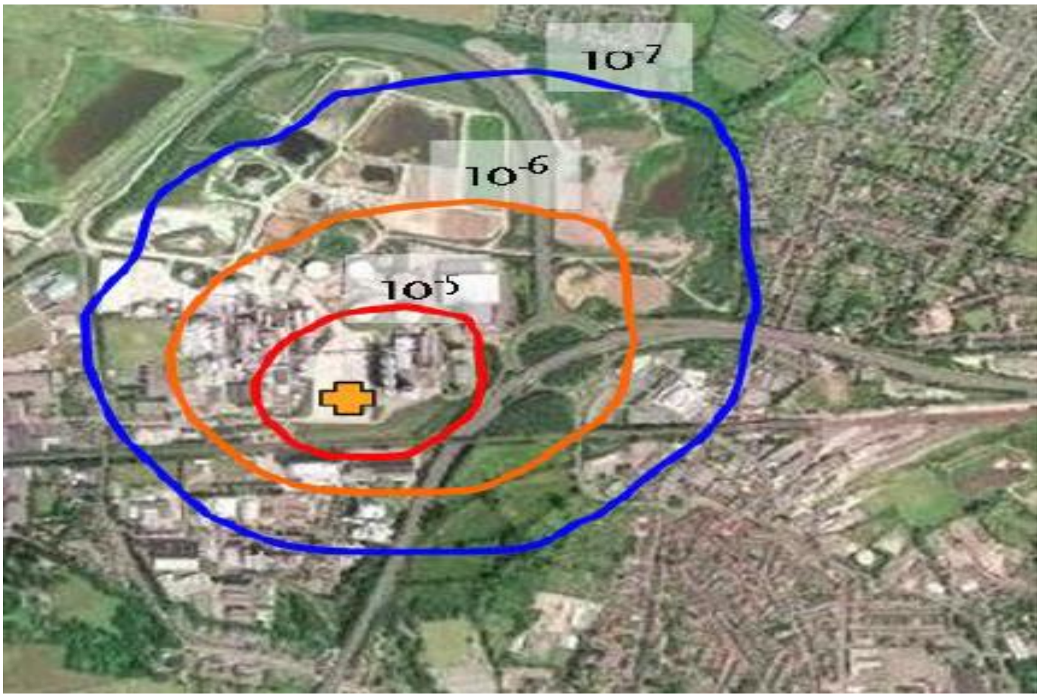
Individual risk (or Cumulative Escalation risk) is the summation of risks from all the outcomes affecting any location and is usually calculated on a grid. Particularly in the present course individual risk has been determined the so-called, meaning the same as determining the risk of death for a person standing outside in a specific location 100% of the time.

This risk is calculated as follows:

Risk in a specific location = Accident frequency x Damage

This risk can be represented in the form of individual risk curves (Iso-contours for specific risk level). This risk indicator is a function of the distance between the exposed person and the different accidents within the establishment, irrespective of the presence of people in the vicinity. After making the calculations (under the guidelines shown in chapter 3.1.), frequency curves 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} yr^{-1} are drawn up (see figure 1.21 as an example).

Figure. 1.21. Example ISO risk curves showing the distribution of location-based (individual) risk surrounding an industrial facility.



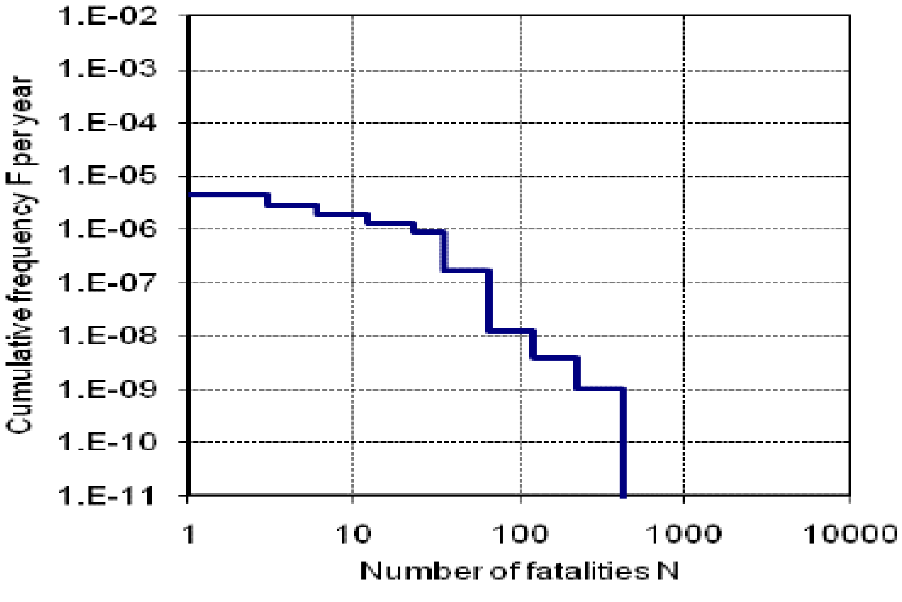
As an example, a person located on a risk curve of death 10^{-6} yr^{-1}, has a death rate of 10^{-6} per year as a result of this industrial activity.

B. Societal risk

Societal risk expresses the risk that a group of people is simultaneously exposed to the consequences of an accident. This is expressed – using an 'FN curve' – as a relationship between the expected frequency of the accident, and the number of people who will die (or be injured) as a result of the accident. 'F' is the (cumulative) frequency of an accident involving more than N deaths3, see Figure 1.22. The result expresses the total expected simultaneous loss to the community. Calculation of an F-N curve takes into account the probability of a number of accident scenarios, and an assessment of how many people might be exposed to consequences under these scenarios, based on population density, places of work, and local protection (whether they are indoors or outdoors). Practices differ regarding the inclusion of the establishments workforce as well as employees at surrounding establishments, or if only the general population is included. Figure 1.22 shows an example societal risk curve. Each step in the curve represents an accident scenario.

Criteria for societal risk and location-based risk are used to complement each other. Criteria for location-based risk are used to determine areas (risk zones) which may not be used for residential or similar purposes, and ensure that individual persons are not exposed to excessive risk. Criteria for societal risk are used to ensure that locations where many people may assemble are not exposed to excessive risk of a major accident, even if they lie outside the risk zones.

Figure. 1.22. Example societal risk curve for an establishment.



In the figure 1.22 The first ‘step’ on the right side of the curve shows the most severe accident scenario (estimated to lead to approx. 400 fatalities, with a frequency of 10^{-9} per year). The second step shows the contribution from the second-most severe accident (estimated to lead to approx. 200 fatalities, with a frequency of $3x10^{-9}$ per year).

1.4. Risk evaluation

Screening criteria are the targets or standards used to judge the tolerability of an identified hazard or effect. They are used to judge the significance of the hazards and effects and together with the results from the risk analysis provide the basis for risk management decision-making. Screening criteria may include adoption of parameters contained in codes and standards.

Screening criteria are normally framed in terms of parameter levels which define the tolerable threshold, based upon the current state of science and technology and the general views of society. Criteria developed by a company to define maximum tolerable risk levels are also screening criteria.

Appropriate screening criteria should be selected when hazards have been identified and should subsequently be used for comparison with the results of the hazards and risk assessment. Failure to achieve a screening criterion identifies an unacceptable condition unless it can be shown that the particular screening criterion is inappropriate in the particular situation. Parameters outside the tolerable range defined in the screening criteria should only be accepted after the consideration and agreement of senior management.

The first principle of risk acceptance is that all unnecessary risk should be removed. This means that the ALARA (As low as reasonable achievable) or ALARP (As low as reasonable practicable) principle are always followed, even where the level of risk already complies with the general risk acceptance criteria. The ALARA principle involves an assessment of whether the costs of a given safety measure are disproportionately large compared to the safety gain. This assessment will be different depending on whether the level of risk is high or low in relation to the risk acceptance criteria. It is therefore not necessary to highlight risk levels where ALARA is especially applicable.

1.5. Risk treatment

In many cases, the measures to control and mitigate hazards and risks are simple and obvious and involve modifications to conform to standard practice. In other cases, alternative measures to reduce risk need to be considered to achieve the best solution. It is important to consider a wide range of possible solutions to the defined hazards, and not to assume that modification of physical facilities is the most appropriate method to control and mitigate risk, e.g. by reducing the frequency and duration of exposure of personnel to risk.

The general hierarchy of risk-reducing measures is

- prevention,
- detection,
- control,
- mitigation,
- emergency response.

Particular attention should always first be given to risk-reducing measures which have the effect of eliminating or reducing the probability of hazardous events occurring. The use of inherently safer design principles to manage risks is preferred. In inherently safer design, the following concepts are used to reduce risk:

- reduction, e.g. reducing the hazardous inventories or the frequency or duration of exposure;
- substitution, e.g. substituting hazardous materials with less hazardous ones (but recognizing that there could be some trade-offs here between plant safety and the wider product and lifecycle issues);
- attenuation, e.g. using the hazardous materials or processes in a way that limits their hazard potential, such as segregating the process plant into smaller sections using ESD valves, processing at lower temperature or pressure;
- simplification, e.g. making the plant and process simpler to design, build and operate, hence less prone to equipment, control and human failure.

Protective measures should be considered after the assessment of possible preventive measures, and should be aimed at mitigating the effects of a hazardous event once it has occurred. Measures to restrict escalation of a hazardous event, together with measures to protect personnel and measures to normalize the situation, may all be considered. Fire and gas detection systems, fire-water systems, active and passive fire protection, temporary refuge, evacuation systems, oil clean-up and recovery equipment and procedures, protective clothing, etc. are all examples of protective measures.

Factors that will influence the selection of measures to reduce the risk include

- the technical feasibility of the risk-reducing measure,
- the contribution of the risk-reducing measure,
- the costs and risks associated with implementing the measure,
- the degree of uncertainty associated with the risk, or the risk-reduction technique, including human factors.

A progressive approach to risk reduction should be adopted, giving attention first to those measures which have greatest effect in risk reduction for least effort. Successive evaluations of risk-reducing measures are undertaken until a point is reached where all the screening criteria have been satisfied (or dispensation has been given by senior management) and no further risk-reducing measures are reasonable.

Risk-reducing measures should be assessed to determine whether they are technically viable and have significant effect. In many situations such assessments can be left to the judgement of the person undertaking the risk management decision-making, who will decide what is satisfactory based upon experience and normal good practice.

In other situations, the effort required to implement a risk-reducing measure in terms of cost, time, difficulty, necessary resources, etc. needs to be considered against the benefit likely to be achieved.

An approach widely used is to evaluate the effort and cost involved in a number of different risk-reducing measures and to estimate the risk-reducing effect of each. By evaluating the cost or effort necessary to arrive at a common level of risk reduction it is often possible to identify those measures which are clearly more effective in risk reduction. In addition, sensitivity analyses should be included as part of a cost-benefit analysis in order to highlight the effect of uncertainties.

The uncertainties associated with cost-benefit analysis are such that the results of such analysis should only be used in conjunction with good engineering judgement when deciding whether or not to implement a risk-reducing measure.

Evaluation of risk-reducing measures should always be based on sound engineering principles and common sense. The following aspects should also be observed: local conditions and circumstances, the state of scientific and technical knowledge relating to the particular situation, and the estimated costs and benefits.

The results of the hazards and risk assessment and the decisions taken in respect to the need for, and role of, any risk-reducing measures should be recorded so that they are available to those who operate the installation and for those involved in any subsequent change to the installation. In ISO 13702, the term used to refer to this record is “strategy”. The level of detail in a strategy needs to be consistent with the stage of the project. In the initial stages it is of necessity relatively brief, setting out general principles and overall requirements, but as the project proceeds it will become more specific.

For a particular installation a number of such strategies may be required. The level of detail in a strategy depends upon the scale of the installation and the stage in the installation life cycle at which the risk management process is undertaken. The strategies should describe the role, and any functional requirements, of each of the systems required to manage possible hazardous events on the installation. ISO 13702 provides guidance on appropriate levels of detail in the strategies.

A focused approach should be used to the specification of functional requirements, with greater attention given to the definition and monitoring of critical equipment, systems and procedures than to less critical elements.

Functional requirements should be verifiable, realistic and achievable, and should be reviewed at specified intervals to ensure their continuing relevance and suitability.

An important principle to be adopted in the setting of functional requirements is that their number and level of detail should be commensurate with the magnitude of the risk to be managed. Thus caution should be exercised to avoid setting functional requirements at a level of detail that makes little contribution to the management of the risks on an installation.

In identifying the systems for which functional requirements are developed, the following factors should be considered:

- the systems selected should make a significant contribution in controlling risk;

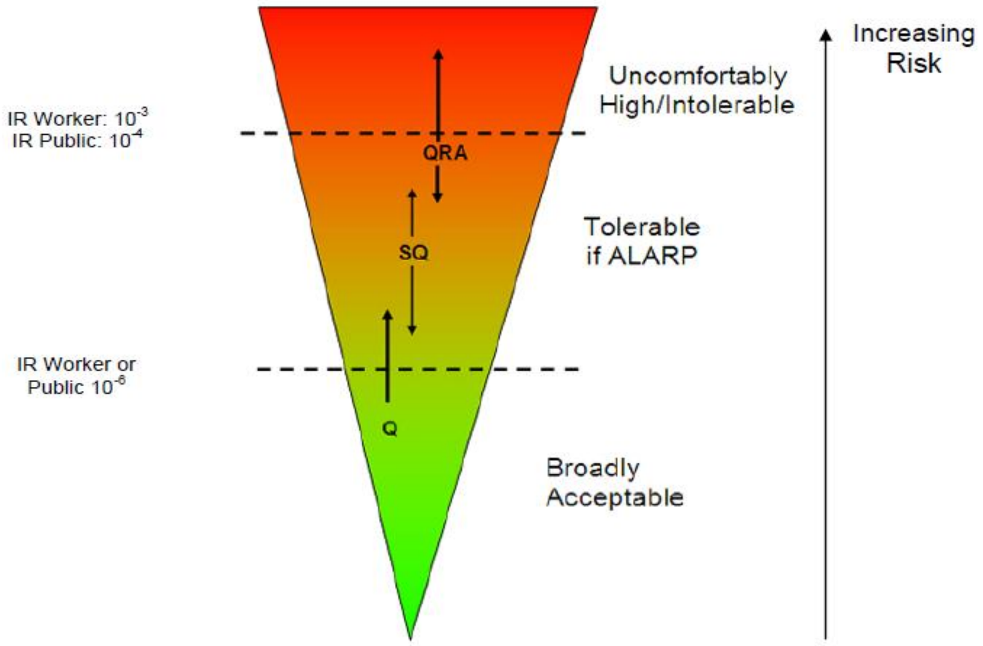
- the parameters selected should be directly relevant to the achievement of the system goals;
- the parameters selected should be capable of verification.

Functional requirements for risk-reducing measures should include

- those parameters which are clearly identifiable and important to fulfil a role in risk reduction;
- procedural or operational criteria, where essential in the control of risk;
- directly verifiable criteria which do not require extensive computational effort;
- recording of data to confirm compliance with functional requirements.

This should, wherever possible, be part of the normal operational and recording tasks associated with the particular activity. This reduces the possibility of duplication of effort and increases the probability that the task will be undertaken in a conscientious and efficient manner.

Figure.1.23. Example of tolerability of risk framework (adapted from SPC/Permissioning/37 - www.hse.gov.uk/foi/internalops/hid/spc/spcperm37/index.htm)



Again, the Screening criteria can be qualitative (see figure 1.6) or be based on quantitative figures (regulatory, corporative…) after doing a QRA. There is no harmonization (not even in Europe) about the Screening criteria, so what it is shown in this part of the course is some internationally accepted criteria.

- The review of practices indicates agreement among the selected EU countries on acceptance criteria for location-based (individual) risk for the general population of 10^{-6} per year.
- Criteria for societal risk only exist in Flanders and the Netherlands. These criteria take the form of a line limiting the F-N curve. In both the Netherlands and Flanders, this line has a slope of 2 (on a double-logarithmic scale). Under the criteria for the Netherlands, risk of accidents involving 10 or more deaths must be less than 10^{-5} per year. In Flanders, the limit is 10^{-4} per year.

The comparison between the risk estimation and the criteria is needed. If the risk is not ALARP, a risk treatment must be done to reduce it.

Exercises Questions for Chapter 1 (Risk Management)

1. Which of this stages are part of the Risk Management process?

a) Risk Assessment

b) Risk Evaluation

c) Risk Treatment

d) All of them

2. Which are the benefits of the risk management?

a) Improve organizational resilience

b) Enhance health and safety performance, as well as environmental protection

c) Maximize losses

d) Establish an unreliable basis for decision making and planning

3. Which of this points are parts of a Safety Management System (field of SEVESO Directive)?

a) Identification and evaluation of major hazards

b) Quality audit

c) Management of change

d) Operational Control

4. Risk estimation can be quantitative, semi quantitative or qualitative. Which of the sentences, about quantitative estimation below are true?

a) The quantitative estimation is done when international or national regulations (or corporative regulations) are compulsory

b) Quantitative estimation is a non-rigorous process to estimate risks.

c) The checklist is the principal background to do a quantitative estimation.

d) The quantitative estimation is done assessing a qualitative o semi quantitative methodology, the risk estimated is over the screening criteria

5. Which of this are Risk identification methodologies?

a) ALARP

b) FMEA

c) HAZOP

d) BLEVE

6. Which can be the reason to classify a hazard as not significant?

a) The effect of realization of a hazard may be included in another more severe hazard.

b) High consequences.

c) Very low frequency of occurrence.

d) High frequency of occurrence but low consequences.

7. Which of this stages are part of the QRA?

a) Identify scenarios

b) Consequence modelling

c) Event tree and frequency analysis

d) Criteria and prioritization

8. Which of this scenarios shall be calculated in a QRA?

a) Release of the entire content of a storage tank in 10 min.

b) Overfilling of a storage tank.

c) Rupture of all pipes at a time in heat exchangers and condensers

d) Outflow of the minimum outflow rate of a pressure relief valve

9. What are the physical effects of a pool fire?

a) Toxicity

b) Thermal radiation

c) Overpressure

d) Direct flame contact

10. What are the physical effects of a BLEVE?

a) Toxicity

b) Missiles (fragments of the storage tank)

c) Thermal radiation

d) Overpressure

11. Which of this are modifiers of the frequency of a critical event?

a) Safety distances

b) Emergency plan and drills

c) Detection and shutdown systems

d) Managements factors

12. On which depends the dose received in a scenario of toxicity?

a) Maximum concentration of the substance in the air

b) Average intensity received, in kW/m

c) Overpressure generated (mbar)

d) Exposure time in seconds

13. Complete the equation: frequency x damage =

a) Risk

b) Consequence

c) Safeguard

d) Effects

14. What does ALARP mean?

a) As low as reasonable achievable

b) As low as reasonable practicable

c) As low as possible

d) As high as reasonable practicable

15. What does Societal Risk express?

a) The highest consequence event for the vicinity

b) Summation of risks from all the outcomes affecting any location

c) Group of people simultaneously exposed to the consequences of an accident

d) It is expressed using a FN curve (frequency vs number of fatalities)

16. Which is the effect causing pulmonary hemorrhage?

a) Thermal radiation

b) Overpressure

c) Toxicity

d) Fragments

17. Which is the most used acceptance criteria in EU countries for individual risk?

a) 10^{-6}

b) 10^{-5}

c) 10^{-7}

d) 10^{-4}

18. In inherently safer design, the following concepts are used to reduce risk:

a) Reduction, e.g. reducing the hazardous inventories or the frequency or duration of exposure;

b) Substitution, e.g. substituting hazardous materials with less hazardous ones (but recognizing that there could be some trade-offs here between plant safety and the wider product and lifecycle issues);

c) Attenuation, e.g. using the hazardous materials or processes in a way that limits their hazard potential, such as segregating the process plant into smaller sections using ESD valves, processing at lower temperature or pressure;

d) All of them

19. Factors that will influence the selection of measures to reduce the risk include

a) Technical feasibility of the risk-reducing measure.

b) Contribution of the risk-reducing measure

c) Degree of uncertainty associated with the risk

d) Production time lost by implementing the measure (checklist, procedures…)

20. Which of these standards can help us to implement a Safety Management System?

a) SEVESO Directive

b) BS ISO 4500

c) ISO 31000

d) RR1035

21. The definition of consequence is “outcome of an event affecting objectives”.

a) True

b) False

22. The definition of Risk Management is “Process of finding, recognizing and describing risks”.

a) True

b) False

23. The HAZOP is the perfect Risk Identification Methodology for installations which are a repeated of earlier designs and where there are recognized codes and standards.

a) True

b) False

24. The acronym of QRA means “Qualitative Risk Assessment”.

a) True

b) False

25. The catastrophic failure of a storage tank is a compulsory scenario to calculate in a QRA.

a) True

b) False

26. Jet fire is an ignition of a continuous leakage of flammable gases or vapours contained in pipes or containers with overpressure.

a) True

b) False

27. The probit equation is independent of the phenomena evaluated.

a) True

b) False

28. The Individual risk (or Cumulative Escalation risk) is the summation of risks from all the outcomes affecting any location and is usually calculated on a grid.

a) True

b) False

29. The screening criteria are the targets or standards used to judge the tolerability of an identified hazard or effect.

a) True

b) False

30. The general hierarchy of risk-reducing measures is: prevention, detection, control, mitigation, emergency response.

a) True

b) False

31. BLEVE is suitable in atmospheric tanks

a) True

b) False

Answers for Chapter 1 (Risk Management)

1. D
2. A and B
3. A, C and D
4. A and D
5. B and C
6. A and C
7. D
8. A and B
9. B and C
10. B, C and D
11. A and C
12. A and D
13. A
14. B
15. C and D
16. B
17. A
18. D
19. A.B and C
20. A and C
21. A
22. B
23. B
24. B
25. A
26. A
27. B
28. A
29. A
30. A
31. B

CHAPTER 2

2. LEGISLATION

2.1. Classification

2.1.1. General

2.1.1.1. Course objectives/identification

The objectives of the course are as follows:

- to learn to know how hazardous materials can be identified on based on their warning signs, symbols, labels and pictograms
- to learn to know how hazardous materials should be marked for safety reasons
- to learn to know the Globally Harmonized System of Classification and Labelling of Chemicals (CLP/GHS) under the European REACH legislation [1-2-3]
- to learn to know the nine ADR classes of hazardous materials

2.1.1.2. Course outcomes

As the outcomes of this course could be mentioned, among other things, the following:

- identifying of hazardous materials and chemicals on the base of warning symbols and labels
- labelling of workplace hazardous chemicals to increase safety
- helping to keep different chemicals separate from each other to prevent dangerous reactions and chemical accidents

2.1.1.3. Classification

Classification is a part of chemical legislation REACH that shifts the responsibility from public authorities to industry with regards to assessing and managing the risks posed by chemicals and providing appropriate safety information for their users.

2.1.1.4. Operation (how it is used)

This training module includes theory and legislation about classification of hazardous chemicals, presentation of different ADR groups and typical chemicals in them. After studying the text section there is a training section about questions to be answered (At the end of this chapter).

2.1.1.5. Pros. and Cons.

A. Pros.

- Hazardous chemicals transported or stored in great amounts can be easily identified on the base of labelling system, and so to get to knows dangers involved to them.
- Classification system helps to store hazardous chemicals properly to prevent accidents.

B. Cons.

- Because of subclasses and categories classification of hazardous chemicals is in reality rather complicated. Especially difficult is classification of chemical mixtures and liquids with varying concentrations.

2.1.2 Definition of hazardous materials

- substances and products that, if not properly handled, can damage people, animals, nature and property.

2.1.3. Amount of chemicals

- over 100 milj. substances are known in the world and each of them has own CAS-number [4].

2.1.4. Classification of hazardous materials according to chemical law

- Combustible and explosive substances (E, O, F+, F)
- Substances dangerous to health (T+, T, Xn, C, Xi, Cars., Muta., Repr.)
- Substances dangerous to the environment (N)

The labels may also contain a code letter indicating the specific nature of the hazard [5].

Table.2.1. Classification of hazardous materials.

E	Explosive
O	Oxidising
F+	Extremely Flammable
F	Highly Flammable
R10	Flammable

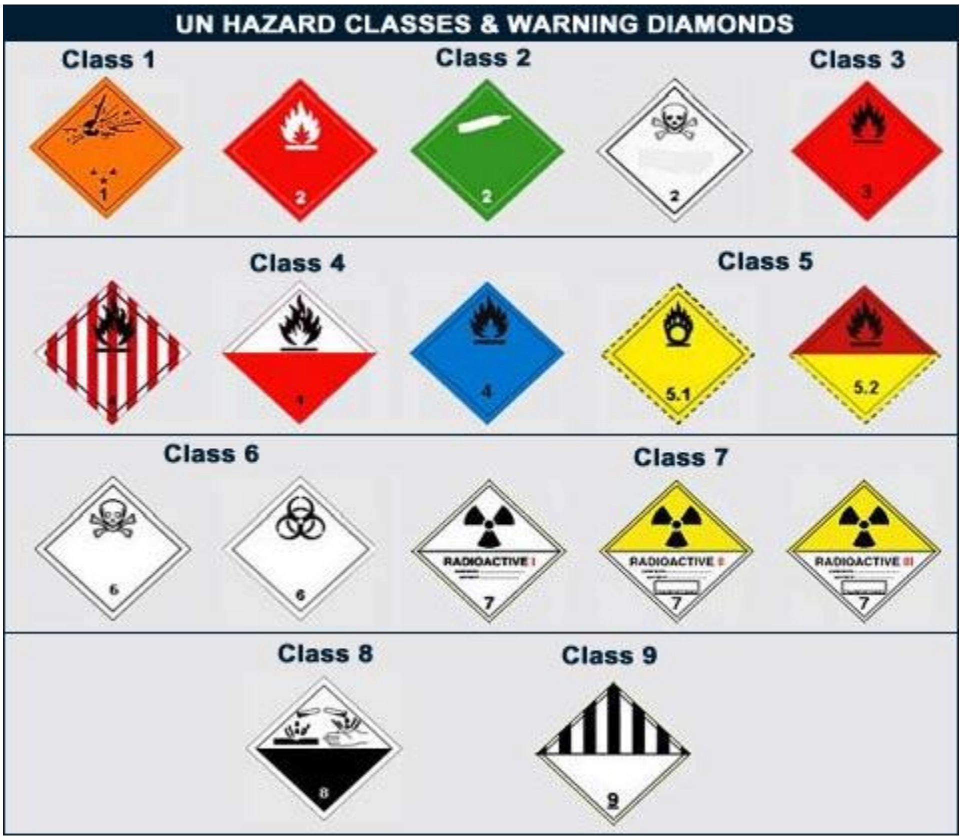
T+	Very toxic
T	Toxic
Xn	Harmful
C	Corrosive
Xi	Irritant
R42 and/or R43	Sensitising
CarcCat(1)	Carcinogenic
MutaCat(1)	Mutagenic
ReprCat(1)	Toxic for reproduction

2.1.5. ADR Classes of hazardous materials [7]

2.1.5.1. Hazard classes

- Class 1 Explosive substances and articles
- Class 2 Gases
- Class 3 Flammable liquids
- Class 4.1 Flammable solids, self-reactive substances and solid desensitized explosives
- Class 4.2 Substances liable to spontaneous combustion
- Class 4.3 Substances which, in contact with water, emit flammable gases
- Class 5.1 Oxidizing substances
- Class 5.2 Organic peroxides
- Class 6.1 Toxic substances
- Class 6.2 Infectious substances
- Class 7 Radioactive material
- Class 8 Corrosive substances
- Class 9 Miscellaneous dangerous substances and articles

Figure.2.1. Symbols for warning of dangerous chemicals [6].



A. Explosive substances (ADR1)

A.1. General definitions [7]

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

A pyrotechnic substance is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions.

An explosive article is an article containing one or more explosive substances.

A pyrotechnic article is an article containing one or more pyrotechnic substances.

A.1.1. Chemical explosions [8]

Deflagration: flame propagation velocity is less than 100 m/s (usually much lower).

Detonation: supersonic exothermic front in excess of 100 m/s up to 2000 m/s.

A.2. Definition of divisions (Cat.1-6)

Division 1.1 Substances and articles which have a mass explosion hazard

- a mass explosion is one which affects almost the entire load virtually instantaneously)
- f. ex. dynamite, trotyl

Division 1.2 Substances and articles which have a projection hazard but not a mass explosionhazard

- f. ex. grenates

Division 1.3 Substances and articles which have a fire hazard and either a minor blast hazard ora minor projection hazard or both, but not a mass explosion hazard

- combustion of which gives rise to considerable radiant heat
- which burn one after another, producing minor blast or projection effects or both
- ex. great fireworks, flash powders

Division 1.4 Substances and articles which present no significant hazard

- substances and articles which present only a small hazard in the event of ignition or initiation.
- f. ex. most fireworks, smokeless powder

Division 1.5 Very insensitive substances which have a mass explosion hazard

- f. ex. ANO = ammonium nitrate + oil

Division 1.6 Extremely insensitive articles which do not have a mass explosion hazard

- articles which contain only extremely insensitive detonating substances and whichdemonstrate a negligible probability of accidental initiation or propagation.

A.3. Labelling and classification of packaging [9]

A.4. Carriage of explosive substances

B. Gases (ADR2)

B.1. Definitions [7]

Gases can be flammable F (2.1.), non-flammable non-toxic A (2.2.), oxidative O, corrosive C (2.3.) or toxic T (2.3.).

A flammable gas is a gas having a flammable range with air at 20 °C and a standard pressureof 101.3 kPa.

- f.ex. hydrogen, methane, acetylene, propane

Non-flammable non-toxic gases are asphyxiant gases which dilute or replace the oxygen normally in the atmosphere

- f.ex. nitrogen, argon, carbon dioxide

An oxidizing gas is any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does

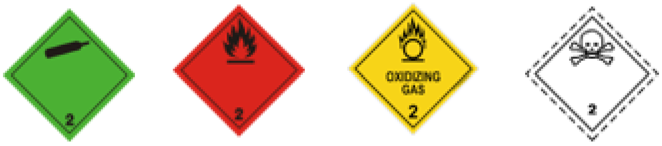
- f.ex. oxygen

Corrosive and Toxic gases are known to be so toxic or corrosive to humans as to pose a hazard to health; or are presumed to be toxic or corrosive to humans because they have an LC_{50} value equal to or less than 5000 ml/m^3 (ppm).

- Corrosive gases are considered to be toxic, and are therefore assigned to the group TC, TFC or TOC.
- f.ex. ammonia, chlorine, sulphur dioxide, NOx, hydrogen cyanide, carbon monoxide.

B.2. Labelling and classification of packaging

B.3. Carriage of gases



Gases can be in cylinders as a) <u>compressed gases</u> (e.g. hydrogen) b) as <u>refrigerated liquids</u> (e.g. liquefied nitrogen) c) as <u>by pressure liquefied gases</u> (e.g. propane) or d) <u>under pressure dissolved gases</u> (e.g. acetylene).

C. Flammable liquids (ADR3)

C.1. Definitions [10]

The GHS classification system simply defines a flammable liquid as a liquid having a flash point of not more than 93°C. A flammable liquid is classified in one of four categories for this class according to the following table:

Table.2.2. GHS categories.

GHS category	**Criteria**
1	Flash point <23°C and initial boiling point < 35°C
2	Flash point <23°C and initial boiling point > 35°C
3	Flash point >23°C and < 60°C
4	Flash point >60°C and < 93°C

Combustible liquids having a flash point >93°C are not classified as hazardous chemicals.

C.2. Labelling and classification of packaging

C.3. Carriage of flammable liquids

Liquids which have a flash point of less than 60°C and which are capable of sustaining combustion.

D. Flammable solids (ADR4)

There are three different subclasses in flammable solids as follows:

- Flammable solids (4.1.)
  - ✓ f.ex. food industrial powders
- Spontaneously combustible materials or self-heating substances (4.2.)
  - ✓ f.ex. white phosphorus, magnesium powder
- Materials that are dangerous when wet or substance which, in contact with water, emit flammable gases (4.3.)
  - ✓ sodium, potassium

D.1. Definitions [7]

A *flammable solid* is a solid which is readily combustible, or may cause or contribute to fire through friction.

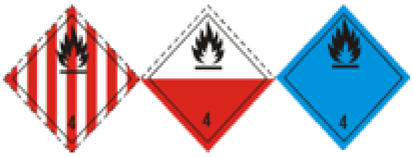
Readily combustible solids are powdered, granular, or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly.

Self -heating of substances, leading to spontaneous combustion, is caused by reaction of thesubstance with oxygen (in the air) and the heat developed not being conducted away rapidly enough to the surroundings. Spontaneous combustion occurs when the rate of heat production exceeds the rate of heat loss and the auto -ignition temperature is reached.

Substance which, in contact with water, emit flammable gases are solid or liquid substances which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

D.2. Labelling and classification of packaging

D.3. Carriage of flammable solids



E. Oxidizing substances (ADR5)

Oxidizing substances can be divided into two main subclasses.

- Inorganic oxidative substances (5.1.)
  - ✓ non combustible
  - ✓ f.ex. hydrogen peroxide, chlorate, chlorite, nitrate
- Organic peroxides (5.2.)
  - ✓ contain both combustible and oxidative material => like explosives
  - ✓ highly explosive when temperature > 80 Celsius
  - ✓ f.ex. dimethyl peroxide

E.1. Definition

E.1.1. Inorganic oxidative substances (5.1)

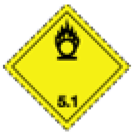
Here oxidizing substance can be liquid or solid which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

E.1.2. Organic peroxides (5.2.)

Organic peroxides are liquid or solid organic substances which contain the bivalent -0-0-structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. Organic peroxides are thermally unstable substances, which may undergo exothermic self-accelerating decomposition.

E.2. Labelling and classification of packaging

E.3. Carriage of oxidative substances



F. Toxic substances (ADR6)

Toxic substances have two subclasses: toxic substances 6.1. and Infectious substances 6.2.

F.1. Toxic substances (Class 6.1.)

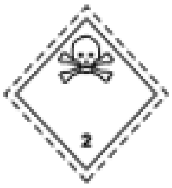
F.1.1. Definitions

Here toxic substances can be solid or liquid. Toxicity can be determined by many ways. Here toxicity has been divided into three classes according to LD50 (lethal dose) values (Hodge and Sterner Scale) [11].

- highly toxic (T+): LD50 <50 mg (rat)
- moderately toxic (T): LD50 50 - 500 mg (rat)
- slightly toxic (harmful) (Xn, Xi): LD50 500 - 5000 mg (rat)

F.1.2. Labelling and classification of packaging

F.1.3. Carriage of toxic substances



F.2. Infectious substances (6.2.)

F.2.1. Definitions [12]

Infectious substances are assigned to the following categories:

- **Category A:** An infectious substance in a form capable of causing permanent disability or life-threatening or fatal disease in otherwise healthy humans or animals.
- **Category B:** An infectious substance that is not in a form generally capable of causing permanent disability or life-threatening or fatal disease in otherwise healthy humans or animals.

F.2.2. Labelling and classification of packaging

F.2.3. Carriage of Infectious substances

G. Radioactive material (ADR7)

G.1. Definitions [13]

There are three different type of radiation as follows:

The extra energy, or radiation, emitted by radioactive elements comes in three different types: alpha, beta, and gamma.

Alpha radiation is a stream of alpha particles, which are positively charged. They're fairly large, which means they have a difficult time getting through materials like clothes and paper.

Beta radiation is a stream of beta particles, which are negatively charged. These particles can more easily penetrate materials like clothes, and they can even get deep into your skin where they can do harm to your cells. But they can be blocked with denser materials like aluminium.

Gamma radiation is high-frequency electromagnetic radiation. Gamma rays have no charge but have A LOT of energy; more energy than even visible light or X-rays.

Because of this, they are able to pass right through most materials, making them quite dangerous. But they can't penetrate very dense materials like lead, which is why you may be given a lead vest for protection in a hospital or laboratory.

G.2. Labelling and classification of packaging

G.2.1. Radioactive White-I

Almost no radiation--0.5 mrem/hr (5 µSv/hr) maximum on surface.

G.2.2. Radioactive Yellow-II

Low radiation levels--50 mrem/hr (0.5 mSv/hr) maximum on surface; 1 mrem/hr (10 µSv /hr) maximum at 1 meter.

G.2.3. Radioactive Yellow-III

Higher radiation levels--200mrem/hr (2 mSv/hr) maximum on surface; a 10 mrem/hr (0.1 mSv/hr) maximum at 1 meter. Also required for fissile class III or large-quantity shipments, regardless of radiation level.

G.3. Carriage of radioactive substances

H. Corrosives (ADR8)

H.1. Definitions [7]

A substance or a mixture that is corrosive to metal is a substance or a mixture which by chemical action will materially damage, or even destroy, metals.

- cause full thickness destruction of intact skin tissue on exposure time of less than 4 hours;
- exhibit a corrosion rate of more than 6.25 mm per year on either steel or aluminium surfaces at 55°C

Examples of substances:

- Acids like sulphuric acids, hydrpchloric acid and nitric acid
- Alkalies like sodium hydroxide, potassium hydroxide

H.2. Labelling and classification of packaging

H.3. Carriage of corrosive to metals

I. Miscellaneous dangerous substances and articles (ADR9)

I.1. Definition

Miscellaneous dangerous goods are substances and articles which during transport present a danger or hazard not covered by other classes. This class encompasses, but is not limited to, environmentally hazardous substances, substances that are transported at elevated temperatures, miscellaneous articles and substances, genetically modified organisms and micro-organisms and (depending on the method of transport) magnetized materials and aviation regulated substances.

E.2. Examples of substances and articles

Commonly Transported Miscellaneous Dangerous Goods

- Dry ice / cardice / solid carbon dioxide
- Expandable polymeric beads / polystyrene beads
- Ammonium nitrate fertilizers
- Blue asbestos / crocidolite
- Lithium ion batteries
- Lithium metal batteries
- Battery powered equipment

- Battery powered vehicles
- Fuel cell engines
- Internal combustion engines
- Vehicles
- Magnetized material
- Dangerous goods in apparatus
- Dangerous goods in machinery
- Genetically modified organisms
- Genetically modified micro-organisms
- Chemical kits
- First aid kits
- Lifesaving appliances
- Air bag modules
- Seatbelt pretensioners
- Plastics moulding compound
- Castor bean plant products
- Polychlorinated biphenyls
- Polychlorinated terphenyls
- Dibromodifluoromethane
- Benzaldehyde

E.3. Labelling and classification of packaging

E.4. Carriage of miscellaneous dangerous substances and articles

2.1.6. Transportation of hazardous materials

Transportation of hazardous materials can be classified according to a mode of transportation as follows [14].

- **ADR** (International Carriage of Dangerous Goods by Road)
- **RID** (International Carriage of Dangerous Goods by Rail)
- **IMDG** (International Maritime Dangerous Goods)
- **IATA-DGR** (International Air Transport of Dangerous Goods)

Above mentioned agreements or regulations set out the requirements for

- classification
- packaging
- labelling
- certification of dangerous goods
- also includes specific vehicle and tank requirements and other operational requirements.

2.1.6.1. Main duties for transportation of dangerous goods

A. Sender

Sender is a company which send the dangerous materials to third party or companies. The sender has important tasks to safe delivery of materials. Sender should properly package, label, mark the material beside this should give information about the general property and loading limitations about the materials to carrier.

B. Forwarder

Forwarder is the responsible director of the loading. He or she has responsibilities about safe loading and preparation of material to safety transportation. Forwarder has tasks which are given below:

- Secure loading of material to vehicle
- Give information and instruction to driver or carrier about material
- Control the packaging (ie. Empty or damaged packaging)
- Check the prohibition about the mixed loading of materials

C. Vehicle driver or carrier

Carrier is an organisation which is undertaking the transportationof dangerous goods. The main tasks of the carrier are transport and delivery of the materials to third person or organisations. Carrier should responsible from the following duties:

- Road security equipment according to regulation
- Provision of vehicle for loading
- control of transport condition

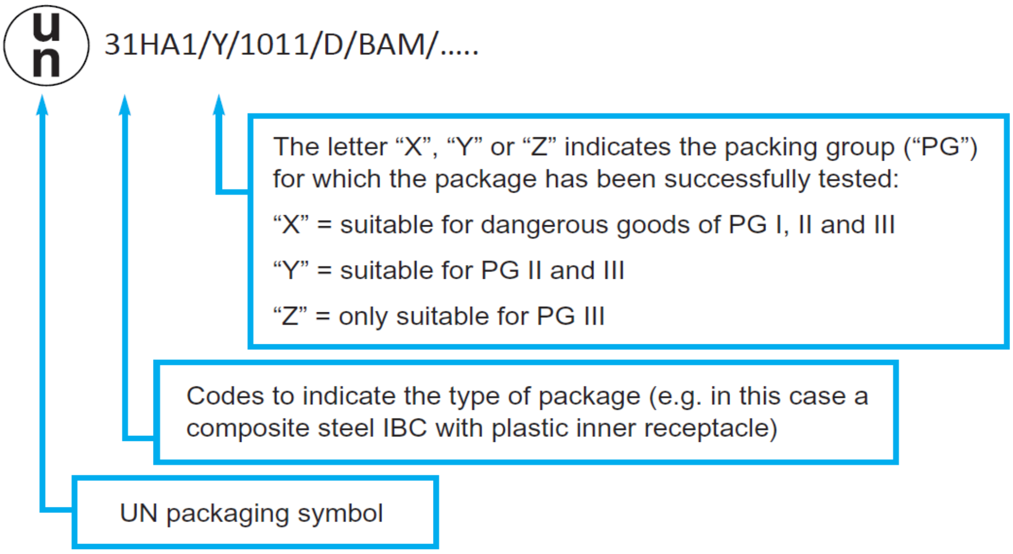
2.1.6.2. Classified with respect to dangerous stage

Dangerous goods can be classified with respect to dangerous stage as follows:

PG I	**high danger**
PG II	**medium danger**
PG III	**low danger**

2.1.6.3. Packaging, marking and hazard labelling

Selecting the correct package type is important for the safe Transportation of dangerous materials. Correct packaging materials for each individual UN numbers.



The letter “X”, “Y” or “Z” indicates the packing group (“PG”) for which the package has been successfully tested:

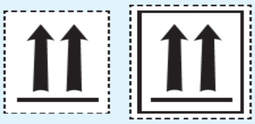
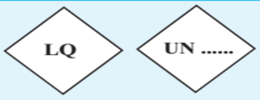
“X” = suitable for dangerous goods of PG I, II and III

“Y” = suitable for PG II and III

“Z” = only suitable for PG III

Codes to indicate the type of package (e.g. in this case a composite steel IBC with plastic inner receptacle)

UN packaging symbol

Marks	Remarks
	Environmentally hazardous substance (EHS) mark Not required for packaging consisting of containers of less than 5 kg/5 l
	Orientation arrows for: • Combination packaging having inner packaging containing liquids • Single packaging fitted with vents • Cryogenic receptacles intended for the carriage of refrigerated liquefied gases Apply on two opposite sides
	Elevated temperature substances mark Applied to tanks, tank-containers etc. Mark is not for packages
	Limited quantity marks (usable up to June 2015)
	Limited quantities mark (except for air transport)
	Limited quantities mark for air transport (accepted in all modes of transport)
	Excepted quantities mark

Packages generally require labels, appropriate mark(s) and a UN number only once on the outer surface of the package. Ideally, if the package size allows, all labels should be displayed on one side, without overlapping or being obscured by other labelling.

When different dangerous goods are packed together in the same outer packaging, the relevant UN numbers and hazard labels/marks must be shown on the outer packaging.

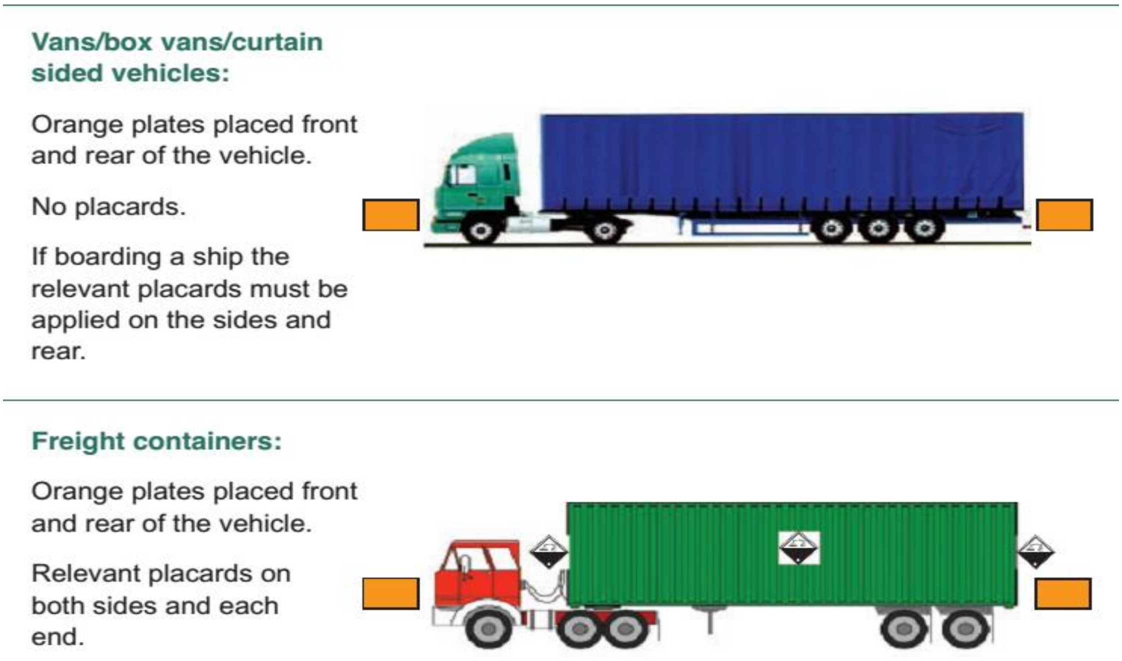
Marking the UN (identification) number of the goods on the package, and the "Proper Shipping Name"

- UN No.: 3082
- Proper shipping name: ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S.

2.1.6.4. Vehicle marking

When vehicles are transporting dangerous goods, they are marked with orange UN number plates (front and rear). When vehicles are carrying containers, the freight container must also be labelled or “placarded” with the appropriate class label on all four sides.

Figure.2.2. Vehicle marking.



Vans/box vans/curtain sided vehicles:

Orange plates placed front and rear of the vehicle.

No placards.

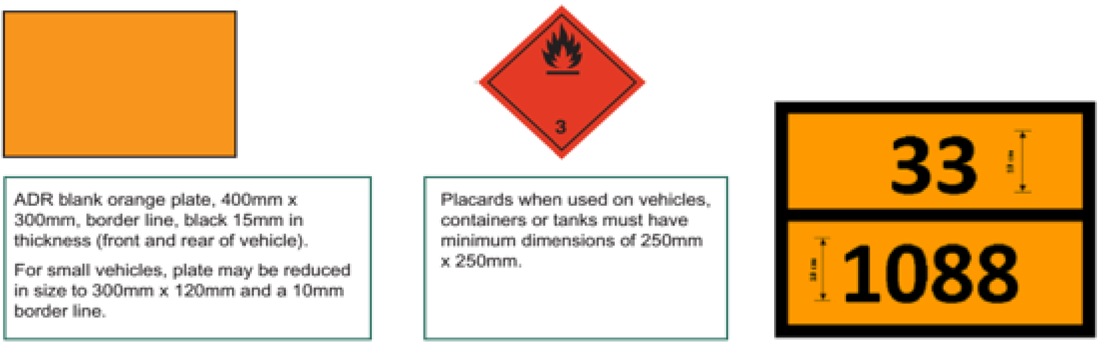
If boarding a ship the relevant placards must be applied on the sides and rear.

Freight containers:

Orange plates placed front and rear of the vehicle.

Relevant placards on both sides and each end.

Figure.2.3. Placards.



ADR blank orange plate, 400mm x 300mm, border line, black 15mm in thickness (front and rear of vehicle).

For small vehicles, plate may be reduced in size to 300mm x 120mm and a 10mm border line.

Placards when used on vehicles, containers or tanks must have minimum dimensions of 250mm x 250mm.

2.1.6.5. Hazard identification number placard [15]

The following identification system is in use for placards in Europe (ADR) for road transport. The background of the placard is orange. The border, horizontal line, and figures are black. Identification numbers are shown in such a way, that the upper number is indicating the danger and the lower number identifies the substances with the UN-number given in the UN Recommendations on the Transport of Dangerous Goods.

A. Hazard identification number

The hazard identification number consists of two or three figures indicating the following hazards:

2 Emission of gas due to pressure or chemical reaction

3 Flammability of liquids (vapours) and gases or self-heating liquid

4 Flammability of solids or self-heating solid

5 Oxidizing (fire-intensifying) effect

6 Toxicity

7 Radioactivity

8 Corrosivity

9 Risk of spontaneous violent reaction

Doubling of a figure indicates an intensification of that particular hazard. Where the hazard associated with a substance can be adequately indicated by a single figure, this is followed by a zero.

If a hazard identification number is prefixed by letter 'X', this indicates that the substance will react dangerously with water.

The hazard identification number combinations have following meanings:

20 inert gas

22 refrigerated gas

223 refrigerated flammable gas

225 refrigerated oxidizing (fire-intensifying) gas

23 flammable gas

236 flammable gas, toxic

239 flammable gas, which can spontaneously lead to violent reaction

25 oxidizing (fire-intensifying) gas

26 toxic gas

265 toxic gas, oxidizing (fire-intensifying)

266 highly toxic gas

268 toxic gas, corrosive

286 corrosive gas, toxic

30 flammable liquid or self-heating liquid

323 flammable liquids which reacts with water emitting flammable gases

X323 flammable liquid which reacts dangerously with water emitting flammable gases

33 highly flammable liquid (flash point below 21°C)

333 pyrophoric liquid

X333 pyrophoric liquid which reacts dangerously with water

336 highly flammable liquids, toxic

338 highly flammable liquids, corrosive

X338 highly flammable liquid, corrosive, which reacts dangerously with water

339 highly flammable liquid, which can spontaneously lead to violent reaction

36 self-heating liquid, toxic

362 flammable liquids, toxic

X362 flammable liquid, toxic, which reacts dangerously with water emitting flammable gases

38 self-heating liquid, corrosive

382 flammable liquids, corrosive, which reacts with water emitting flammable gases

X382 flammable liquid, corrosive, which reacts dangerously with water emitting flammable gases

39 flammable liquids, which can spontaneously lead to violent reaction

40 flammable self-heating solid

423 solid, which reacts with water emitting flammable gases

X423 flammable solid, which reacts dangerously with water emitting flammable gases

44 flammable solid, in molten state, at elevated temperature

446 flammable solid, toxic, in molten state, at elevated temperature

46 flammable or self-heating solid, toxic

462 toxic solid, which reacts with water emitting flammable gases

48 flammable or self-heating solid, corrosive

482 corrosive solid, which reacts with water emitting flammable gases

50 oxidizing (fire-intensifying) substance

539 flammable organic peroxide

55 strongly oxidizing substance

556 strongly oxidizing substance, toxic

558 strongly oxidizing substance, corrosive

559 strongly oxidizing substance, which can spontaneously lead to violent reaction

56 oxidizing substance, toxic

568 oxidizing substance, toxic, corrosive

58 oxidizing substance, corrosive

59 oxidizing substance which can spontaneously lead to violent reaction

60 toxic or harmful substance

63 toxic or harmful substance, flammable (flash point between 21°C and 55°C)

638 toxic or harmful substance, flammable (flash point between 21°C and 55°C), corrosive

639 toxic or harmful substance, flammable (flash point between 21°C and 55°C), which can spontaneously lead to violent reaction

66 highly toxic substance

663 highly toxic substances (flash point not above 55°C)

68 toxic or harmful substance, corrosive

69 toxic or harmful substance, which can spontaneously lead to violent reaction

70 radioactive material

72 radioactive gas

723 radioactive gas, flammable

73 radioactive liquid, flammable (flash point not above 55°C)

74 radioactive solid, flammable

75 radioactive material, oxidizing

76 radioactive material, toxic

78 radioactive material, corrosive

80 corrosive or slightly corrosive substance

X80 corrosive or slightly corrosive substance, which reacts dangerously with water

83 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C)

X83 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which reacts dangerously with water

839 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which can spontaneously lead to violent reaction

X839 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which can spontaneously lead to violent reaction and which reacts dangerously with water

85 corrosive or slightly corrosive substance, oxidizing (fire-intensifying)

856 corrosive or slightly corrosive substance, oxidizing (fire-intensifying) and toxic

86 corrosive or slightly corrosive substance, toxic

88 highly corrosive substance

X88 highly corrosive substance, which reacts dangerously with water

883 highly corrosive substances, flammable (flash point between 21°C and 55°C)

885 highly corrosive substances, oxidizing (fire-intensifying)

886 highly corrosive substances, toxic

X886 highly corrosive substance, toxic, which reacts dangerously with water

89 corrosive or slightly corrosive substance, which can spontaneously lead to violent reaction

90 miscellaneous dangerous substance

B. UN Number

UN number is four-digit numbers that identify hazardous substances, and articles (such as explosives, flammable liquids, toxic substances, etc.) in the framework of international transport. Some hazardous substances have their own UN numbers (e.g. acrylamide has UN2074), while sometimes groups of chemicals or products with similar properties receive a common UN number (e.g. flammable liquids, not otherwise specified, have UN1993 [16].

List of UN numbers can be found on the web address given in the references [17].

C. Tank marking

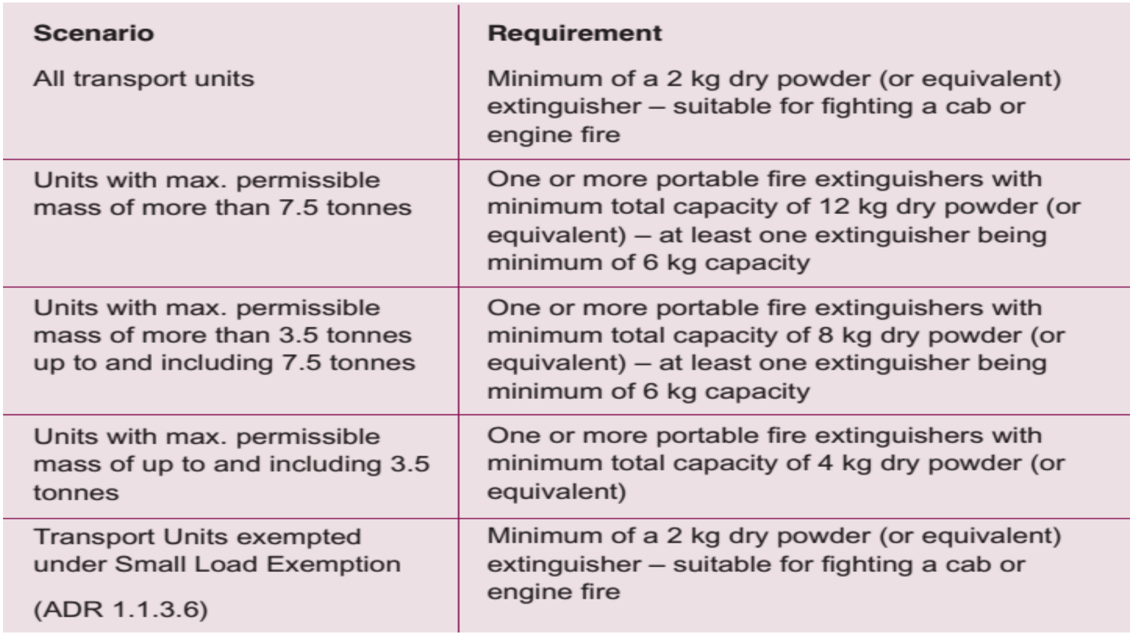
C.1. General provisions

The ADR, RID, IMDG, IATA-DGR set out various requirements for transport, not least requirements for vehicles, packages, tanks, in bulk and containers.

- mixed load restriction
- mixed packing restrictions
- tunnel restrictions
- parking restrictions etc.

- loading, unloading

C.2. Vehicle safety equipment/personal protective equipment



Scenario	Requirement
All transport units	Minimum of a 2 kg dry powder (or equivalent) extinguisher – suitable for fighting a cab or engine fire
Units with max. permissible mass of more than 7.5 tonnes	One or more portable fire extinguishers with minimum total capacity of 12 kg dry powder (or equivalent) – at least one extinguisher being minimum of 6 kg capacity
Units with max. permissible mass of more than 3.5 tonnes up to and including 7.5 tonnes	One or more portable fire extinguishers with minimum total capacity of 8 kg dry powder (or equivalent) – at least one extinguisher being minimum of 6 kg capacity
Units with max. permissible mass of up to and including 3.5 tonnes	One or more portable fire extinguishers with minimum total capacity of 4 kg dry powder (or equivalent)
Transport Units exempted under Small Load Exemption (ADR 1.1.3.6)	Minimum of a 2 kg dry powder (or equivalent) extinguisher – suitable for fighting a cab or engine fire

C.3. Documentation

- Documentation is an important aspect of the transport of dangerous goods. Vital information on the dangerous goods carried, verification of driver qualifications and emergency information are central to the documentation which must be in place during transport operations.
- The transport document detailing all the dangerous goods carried

ADR transport document
Consignor: Company XYZ
Address: A Road, Town, County/Country
Date: dd/mm/yy

Dangerous goods description:	**No. of packages/type**	**Total quantity**
UN1134, chlorobenzene, 3, PG III, (D/E)	20 x 200 litre plastic drums (1H2)	4,000 litre
UN1760, corrosive liquid, N.O.S.(contains sodium hydroxide), 8, PG III, (E)	10 X 10 litre plastic drums (1H1)	100 litre

Consignee(s): Company ABC

Address: A Road, Town, County/Country

C.4. Vehicle packing certificate

CONTAINER/VEHICLE PACKING CERTIFICATE

I hereby declare that the goods described above have been packed/loaded into the container/vehicle identified above in accordance with the applicable provisions of ADR/IMDG Code 5.4.2

MUST BE COMPLETED AND SIGNED FOR ALL CONTAINER/VEHICLE LOADS BY PERSON RESPONSIBLE FOR PACKING/LOADING

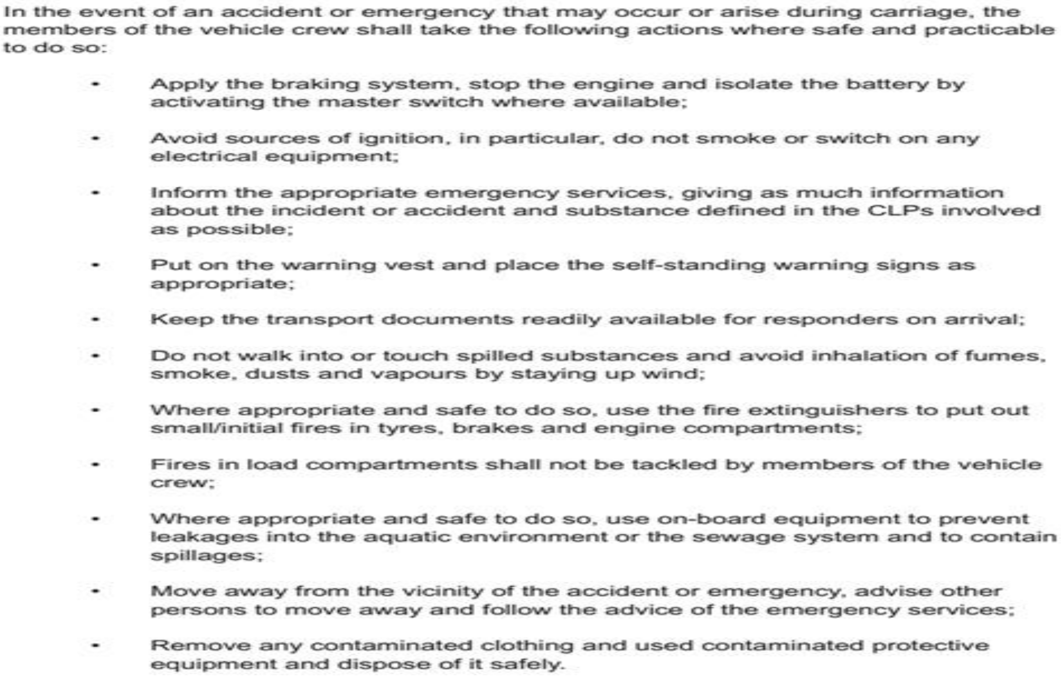
Name of company

Name/status of declarant

Place and date

Signature of declarant

C.5. The instructions in writing for driver or crew



In the event of an accident or emergency that may occur or arise during carriage, the members of the vehicle crew shall take the following actions where safe and practicable to do so:

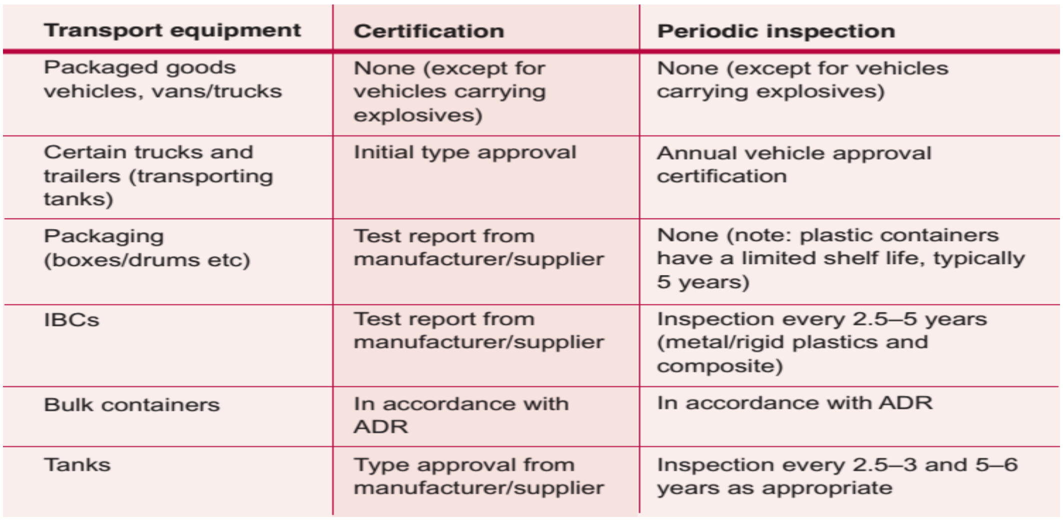
- Apply the braking system, stop the engine and isolate the battery by activating the master switch where available;
- Avoid sources of ignition, in particular, do not smoke or switch on any electrical equipment;
- Inform the appropriate emergency services, giving as much information about the incident or accident and substance defined in the CLPs involved as possible;
- Put on the warning vest and place the self-standing warning signs as appropriate;
- Keep the transport documents readily available for responders on arrival;
- Do not walk into or touch spilled substances and avoid inhalation of fumes, smoke, dusts and vapours by staying up wind;
- Where appropriate and safe to do so, use the fire extinguishers to put out small/initial fires in tyres, brakes and engine compartments;
- Fires in load compartments shall not be tackled by members of the vehicle crew;
- Where appropriate and safe to do so, use on-board equipment to prevent leakages into the aquatic environment or the sewage system and to contain spillages;
- Move away from the vicinity of the accident or emergency, advise other persons to move away and follow the advice of the emergency services;
- Remove any contaminated clothing and used contaminated protective equipment and dispose of it safely.

The annual vehicle certificate of approval;

- The driver's training certificate;
- A copy of any exemptions

C.6. Transport equipment inspection and certification

- Certain transport equipment may require certification and may also be subject to periodic inspection. All inspection and certification regimes must be in accordance with ADR, RID, IMDG, IATA-DGR as appropriate.



Transport equipment	Certification	Periodic inspection
Packaged goods vehicles, vans/trucks	None (except for vehicles carrying explosives)	None (except for vehicles carrying explosives)
Certain trucks and trailers (transporting tanks)	Initial type approval	Annual vehicle approval certification
Packaging (boxes/drums etc)	Test report from manufacturer/supplier	None (note: plastic containers have a limited shelf life, typically 5 years)
IBCs	Test report from manufacturer/supplier	Inspection every 2.5–5 years (metal/rigid plastics and composite)
Bulk containers	In accordance with ADR	In accordance with ADR
Tanks	Type approval from manufacturer/supplier	Inspection every 2.5–3 and 5–6 years as appropriate

C.7. Checklist for transportation

Before the loading and transportation of the materials following statements should be checked.

- Documentation
- Vehicle and its load (from visual inspection of the vehicle itself), packaging, container, tank-containers, bulk container, portable tank, etc.
- Training certificate of the driver
- Transport and safety equipment carried on the vehicle

After checking these subjects, loading of the material on vehicle is important. In this part following conditions should be controlled carefully

- Orientation arrows on packages are pointing in the right direction
- As far as possible liquids are loaded below dry goods
- Load distribution ensure weight is as evenly distribute as possible
- Goods are protected while stacking and no over stacking

2.2. Regulation

2.2.1. CLP

2.2.1.1. General

A. Course objectives/identification

The objectives of the course are as follows:

- to learn to know how hazardous chemicals classified
- to learn to know the Globally Harmonized System of Classification and Labelling of Chemicals (CLP/GHS)
- to learn physical properties, health and environmental effects of hazardous chemicals
- to learn to know how hazardous materials can be labelled and packaged according to CLP Regulation

B. Course outcomes

As the outcomes of this course we provide;

- explanations, methods, read-across tables and calculations to classify substances and mixtures
- labelling and packaging of hazardous chemicals according to CLP Regulation
- protection human health and environment effected by the hazardous chemicals

C.Classification

The Regulation on Classification, Labelling and Packaging of substances CLP – EC / 1272/2008 came into force in 2009 in all member states of the European Union. CLP aims to facilitateworldwide trade by harmonizing criteria for classification and labelling according to the “GloballyHarmonized System of Classification and Labelling” of the United Nations.

D.Operation

During this course, we provide explanations, methods, read-across tables and calculations to classify hazardous substances and mixtures and then how to labelled packaged according to CLP. After studying the text section there is a training section about questions to be answered (at the end of this chapter).

E.Pros. and Cons.

E.1. Pros.

The Regulation on Classification, Labelling and Packaging of substances CLP – EC No. 1272/2008came into force in all member states of the European Union.

CLP aims to provide protection human health and environment against negative effects which may arise from substances, preparations and articles in the market and to arrange their administrative and technical requirements regarding.

E.2. Cons.:

Classifications of hazardous chemicals, especially for mixture, complicated, are mainly done by classifiers.

2.2.1.2. Definition of CLP

A. General

Controlling the chemical risks, knowing and being able to determine the properties of chemicals and their harm to the environment and human health is required to safely produce, use, transport and destroy chemicals. Since chemicals carry lots of dangers and this information is not accessible by all users, it has become necessary to organize this information, which is extremely complex due to the properties of the chemicals, in a systematic way to contain the damages and precautions that the user can understand. All the classification and labelling systems serve this purpose.

United Nations Global Harmonized System (GHS) provides a structure for the inclusion of globally identical physical, environmental, health and safety information of hazardous chemicals, through harmonization of the classification and labelling criteria for Classification and Impact of Chemicals.

For production, use, storage, transport and disposal of chemical wastes and precautions to be taken in the repair and maintenance of chemical containers, The International Labour Organization (ILO) 1990 gives the rules with “Contract No. 170 on Use of Chemicals Safety " and "Recommendation No 177 ".

The first issue of the GHS was adopted by the Sub-Committee on Global Harmonization (SCEGHS) of Classification, Packing and Marking of Chemicals in December 2002 and entered into force. GHS was revised by The United Nations specialist’s committee and published in 2005. In 2006, explosives were added and classified as a second revision with the addition of classification of toxic gases and mixtures. In 2008, ozone layer exposure was rolled to third revision which is still in progress.

The work on the classification and labelling of chemical risks in the European Union is based on the Directive 67/548 / EEC on Hazardous Substances Directive (DSD) published in 1967. In 1988, the Directive on Hazardous Substances Directive 88/379 / EEC entered into force.1991 / 155 / EEC The Safety Data Sheet Directive has mandated the preparation of material safety data sheets together with hazardous chemicals. EEC on published Hazardous Substances Directive (DSD) published in 1967. In 1988, the Directive on Hazardous Substances Directive 88/379 / EEC entered the European Union based on the Directive 67/548 Into force.1991 / 155 / EEC The Safety Data Sheets.

Substances and mixtures that are traded is not only an issue relating to the internal (EU/EEA) market, but also to the global market. Criteria for classification and labelling together with general principles of their application were carefully developed and harmonized within the United Nations (UN) structure, with a scope to facilitate worldwide trade while protecting human health and the environment. The result is; the Globally Harmonized System of Classification and Labelling of Chemicals the first edition of which was adopted in 2002.

As the Union confirmed its intention to contribute to the global harmonisation of criteria classification a labelling through the incorporation of the internationally agreed GHS criteria into Union law, the CLP Regulation follows various declarations where by Enterprises should benefit from the global harmonization of rules for classification an labelling and from consistency between as well as, the rules classification and labelling for supply and use and, on the other hand, those transport.

The version of CLP to which this guidance currently refers is that based on the 4th revision of the GHS.CLP additionally takes some features and procedures from the previous EU system of classification and labelling, represented by the Dangerous Substances Directive (DSD) and the Dangerous Preparations Directive (DPD) that are not part of GHS. Therefore, CLP is similar to, but not identical to the way in which GHS is introduced into the legal framework of countries outside the EU.

The CLP Regulation is legally binding for the Member States. It is directly applicable to all industries and sectors. DSD and DPD are no longer used. These directives, after a transitional period, were repealed, on 1 June 2015.

B. CLP Transition calendar

The European Parliament and Council Decision EC / 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures was published on 31.12.2008 and entered into force in 2009.

Companies operating in the EU member states, producing or importing chemicals and mixtures, have the obligation to classify, label and package such substances and mixtures according to the CLP Regulation on the principles and procedures. The CLP Regulation replaces the Dangerous Goods and Hazardous Mixtures directives. The classification and labelling information of chemical substances, manufacturers and importers in the European Union was notified to the European Chemicals Agency by 1.10.2011. The classification and labelling information in the "Safety Data Sheets", which are the main objective of the communication requirements of the REACH regulation, has to be prepared taking into consideration the transitional periods together with the procedures and principles specified in the CLP Regulation.

For the suppliers to adopt changes to their products to the new system, CLP is being introduced gradually over a number of years. Some products have already been moved over to the new system, and the rest will need to be changed by 1 June 2015, some stocks of products already in the supply chain may be on ward supplied without needing to be relabelled for a further 2 years after deadline.

Figure.2.4. Calendar to the CLP.

Table.2.3. Timetable for substances and mixtures.

Substances	All substances must be classified and labelled according to CLP.Both CLP and DSD classifications must appear on the SDS.	All substances classified and labelled to CLP.Only CLP classifications need appear on the SDS.
	2 year derogation , to allow stocks already on the market to be onward supplied.	
Mixtures	May be classified and labelled according to either DPD or	All mixtures classified

	CLP.If labelled according to CLP,both DPD and CLP classifications must appear on the SDS.	and labelled to CLP.Only CLP classifications need appear on the SDS.
		2 year derogation , to allow stocks already on the market to be onward supplied.

C. Similarities and differences from DSD/DPD

CLP has mostly similarity with The Dangerous Substances Directive (DSD) and the Dangerous Preparations Directive (DPD) that they all deal with classification, labelling and packaging. The hazard pictograms and phrases used in the current system have changed. So the hazard symbols used in DSD / DPD have been changed to the hazard pictograms in the CLP Regulation.

Figure.2.5. Similarities and differences from DSD/DPDto GHS.

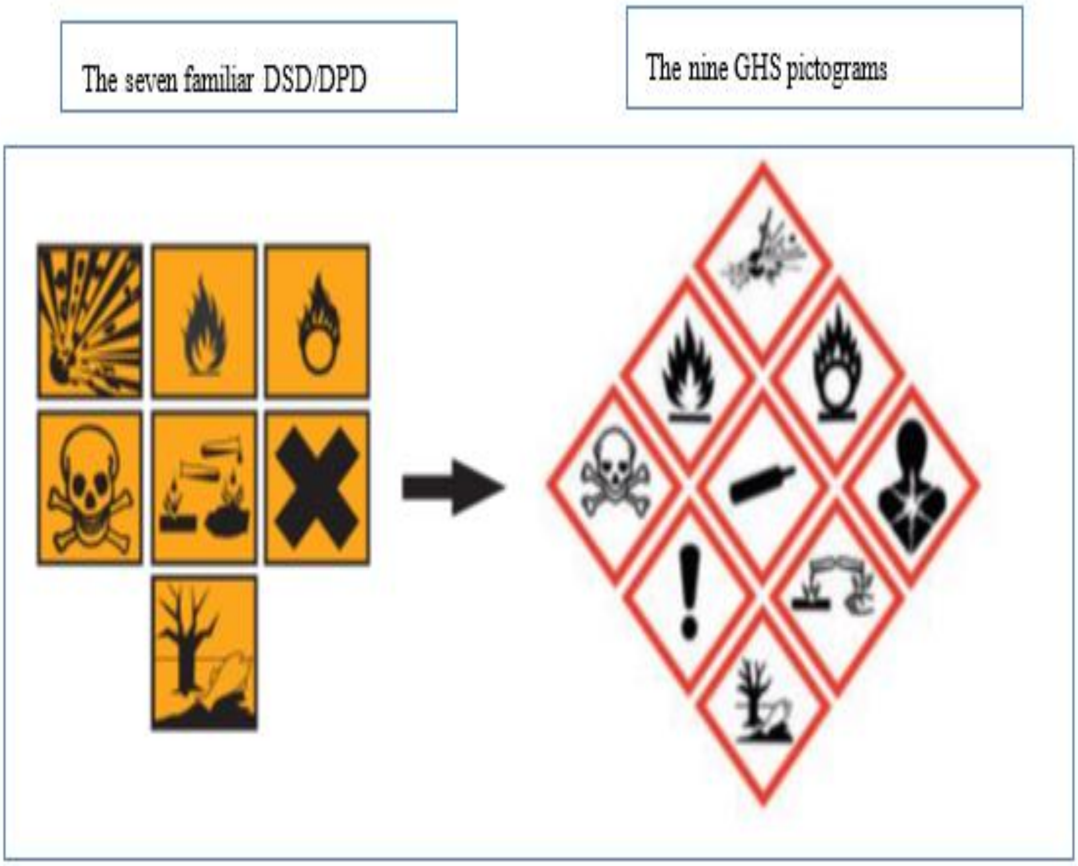


Table.2.4. Types of hazards (according to CLP and DSD/DPD).

Type of hazard	**DSD/DPD symbol**	**CLP pictogram**
May cause serious long-term such as carcinogenicity, mutagenicity reproductive toxicity, respiratory sensitisation ,specific target organ toxicity and aspiration hazard.		
Less serious health hazards such irritants, skin sensitizers and less severe toxicity		
Contains gases under pressure	No symbol under the DSD and DPD	

The terms used in CLP are very similar to those used in the DSD and DPD but not identical.

Table.2.5. Key terms compared table.

Terms Used	**CLP**	**DSD /DPD**
Mixture /s	"A solution composed of two or more substances" *This term means the same as "preparation" under DPD.* *The CLP (and REACH) definition of a mixture differs slightly from that of UN GHS which may well be applied outside of the EU.*	*Term not used in DPD identical to definition of "preparation" in DPD.*
Hazardous	A substance or a mixture fulfilling the criteria relating to physical hazards, health hazards or environmental hazards, laid down CLP is hazardous.	*Term not used in DSD or DPD. Similar to term "dangerous" in DSD.*
Hazard class/hazard category	The nature / severity of a physical, health of environmental hazard.	*Term not used in DSD/DPD. The terms" Category of Danger" was used with a similar meaning.*

Pictogram	A graphical composition that includes a symbol plus other graphic elements, such as a border, background pattern or colour specific information on the hazard concerned. 	*Term not used in DSD. Similar but not identical to the danger symbols used under DSD and DPD.*
Signal Word	The words “Danger” or “ Warning” are used to indicate the severity of the hazard.	*No equivalent in DSD or DPD.*
Hazard statement	Hazards statements describe the nature of the hazards of a substance or mixture, including, where appropriate the degree of hazard. For example,H315	*Term not used in DSD/DPD; instead, “risk phrase” was used. Similar, but not identical to the risk phrases used under DSD.*
Precautionary statement	A description of the measure or measures recommended to minimise or prevent adverse exposure to a hazardous substance or mixture due to its use.	*Term not used in DSD or DPD; instead “safety phrase” was used. Similar but not identical to the safety phrases under DPD.*
Supplier	Any manufacturer, importer, downstream user or distributor placing on the market a substance, on its own or in a mixture ,or a mixture see also chapter 2 of this guidance document.	*Term nut used in DSD or DPD*
Substance(s)	A chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any identified impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.	*Chemical elements and their compounds in the natural state or obtained by any production process, including any additive necessary to preserve the stability of the mixtures and any impurity deriving from the process used ,but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.*

D. Roles and obligations CLP

The obligations given to suppliers of substances or mixtures according to CLP will mostly depend on their role as a substance or mixture in the supply chain. For this reason, it is very important that you define your role within the CLP.

Table.2.6. Identifying the roles under CLP.

Descriptions	Your role under CLP
A naturel or legal person established within the EU who produces or extracts a substance in the natural state within the EU	Manufacturer
A natural or legal person established within the EU who is responsible for the physical introduction into the customs territory of the EU	Importer
A naturel or legal person established within the EU, other than the manufacturer or the importer ,who uses a substance, either on its own or in a mixture, in the course of his industrial or professional activities	Downstream User (including formulator /reimported)
A natural or legal person established within the EU, including a retailer, who only stores and places on the market a substance, on its own or in a mixture, for third parties.	Distributor(including retailer)
A natural or legal person who makes or assembles an article within the EU ;where an article means an objects which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition.	Producer of articles

2.2.1.3. Classification

A. Classifying substances

A.1. What is classification?

Classification of chemicals is according to their potential danger, whether it is irritating, causing cancer, flammable etc.

This is done since people using them –either in industry or as a consumer- have to know their properties as well as dangers to human health, environment etc so against that harm.

Classification is to define hazards; it does not control potential risks. It is about getting information about the chemical concerned and then getting the information needed for decisions to make risk control, so that it can be produces, transported, used and disposed safely.

To manage chemicals safely this is a must. And it has to be done on robust and adequate data/information

A.2. What is hazard?

The potential and capacity of a chemical to cause harm is known as 'hazard'. Chemicals in our daily life are dangerous but most of them can be used without any problem. Ability of a chemical to cause danger does not mean that it will cause harm.

A.3. Who can make the classification?

Classification is the responsibility of chemical suppliers – e.g. manufacturers, importers, downstream users, and possibly distributors.

Basic classification for a chemical is for the suppliers to define whether the chemical is hazardous according to international standards-agreed set of rules (known as 'criteria') to identify what harm a chemical might cause.

There are criteria for:

- physical hazards (e.g. explosivity, corrosivity, etc.);
- health hazards (e.g. potential to cause cancer in humans, to irritate the skin or eyes, etc.); and
- environmental hazards (e.g. harmful to the aquatic environment, etc.).

When classifying a chemical, the supplier must consider:

- what sort of harm a chemical might cause – the hazards,
- how certain it is that the chemical could actually have this effect,
- how serious the effect might be, and
- how potent the chemical is.

Classification of a mixture is generally based on what is known of the constituent substances or similar products.

A.4. What is a harmonised classification?

When classification is agreed by the experts at Europe, and made mandatory by the ruling laws, this is a harmonized classification.

The most common substances are classified by harmonization.

This type of classification is legally binding and suppliers are obliged to used them.

These substances are listed in Annex VI of the CLP Regulation. This list is updated with scientific and technical developments.

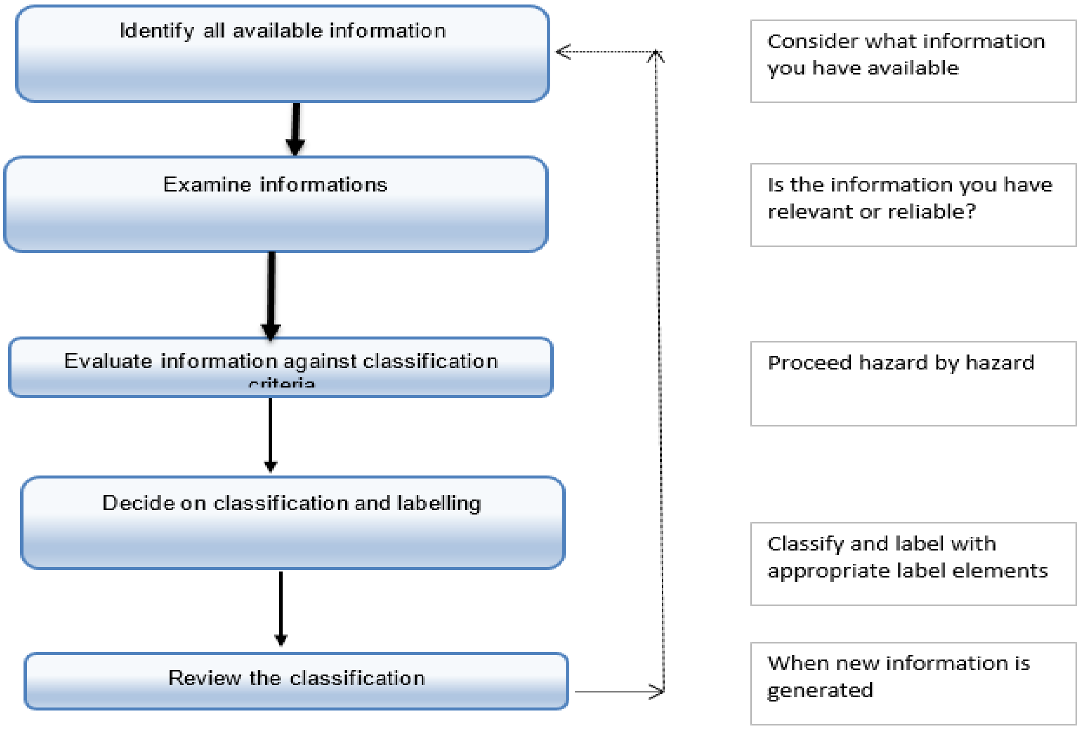
Chemical classification is used to regulate the supply and use of chemicals.

In some cases, classification can act as the basis for requiring additional chemical controls, protective measures, or restrictions on sale or use. This is usually the case where the chemicals are particularly harmful, where they may have the chance of effecting a wide population or the environment because of the volumes involved, and where the chemicals are used in the workplace.

B. How to classify

There are five basic steps for classifying substances, as set out in Figure 2.6.

Figure.2.6. Basic Steps for classifying substances.



B.1. Get all available information

To identify the hazard identification, information is needed for chemicals and each chemical in mixtures:

B.1.1. Chemical identification

- Chemical name with synonyms;
- the Chemical Abstracts Services (CAS) Registry Number (if available); and
- any other information that reveals the precise chemical designation and composition of the substance, such as impurities and stabilizers.

B.1.2. Physical and chemical properties

- The physical and chemical properties of a hazardous chemical are the empirical data of the substance or mixture. That is, this data has been gathered from observation or by tests performed on the chemical in accordance with the Test Method Regulation [2] (EC) No 440/2008.
- Concentration of substances in the mixture.

B.1.3. Health effects

For some hazard classes and categories in the GHS, authorities are given an option of which concentration cut-off value to use.

B.2. Health hazards

Acute toxicity, Skin corrosion/irritation, Serious eye damage/eye irritation, Respiratory or skin sensitization, Germ cell mutagenicity, Carcinogenicity, Reproductive toxicity, Specific target organ toxicity – single exposure, Specific target organ toxicity – repeated exposure, Aspiration hazard, Biohazardous infectious materials

Note: Your information source should be primarily your suppliers.

B.3. Examine information/cross check

The second step in the hazard classification process is data analysis. Make data analysis, which is demanding in terms of technical expertise. For both health and physical hazards, explicit classification criteria are provided in the Hazard standard. For example, criteria are given for classifying a chemical as a flammable liquid, an organic peroxide, and for designating a chemical as acutely toxic or a carcinogen

B.4. Evaluate information and classification criteria

Check if the information clues about a hazardous property. This must be done by an expert. Is the information comparable to hazard criteria? This exercise must be repeated for each hazard class defined under CLP.

B.5. How to decide on classification and labelling

If the substance holds the criteria for particular hazard, then you must assign respective classification (hazard class and category) and the appropriate labelling elements for the label and/or the safety data sheet, i.e. the signal words, hazard statements, hazard pictograms and precautionary statements.

B.6. Review the classification

Classifiers shall be aware of updates to chemical SDS's and changes to classifications with all available information sources.

B.6.1. Mixtures

For some mixtures, it may not be possible to directly translate its hazardous substance classification into a GHS classification because of differences in cut-off concentrations used in the Approved Criteria and the GHS. In these cases, additional steps may be required.

Where the mixture itself has been tested then the data on the mixture should always be used to classify the mixture in preference to calculations based on individual ingredients.

If there is no available test data or information on the mixture itself, then it is essential to obtain the list of ingredients and their percentage content in the mixture so that the correct GHS classification of the mixture can be determined.

Using the hazard classification for each ingredient in the mixture, the mixture's classification can be determined using the criteria and decision logic described in Globally Harmonized System for each hazard class.

In the CLP Directive, three categories are considered when classifying substances or mixtures

- Physical
- Human health

- Environmental

B.6.2. Hazard pictograms

Form part of the international Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Two sets of pictograms are included within the GHS: one for the labelling of containers and for workplace hazard warnings, and a second for use during the transport of dangerous goods. Either one or the other is chosen, depending on the target audience, but the two are not used together. The two sets of pictograms use the same symbols for the same hazards, although certain symbols are not required for transport pictograms. Transport pictograms come in wider variety of colours and may contain additional information such as a subcategory number.

2.2.1.4. CLP hazard classes and categories

Table.2.7.CLP Hazard classes and categories.

PHYSICAL HAZARDS
Explosives (Unstable explosives, Divisions 1.1 ,1.2,1.3,1.4,1.5 and 1.6)
Flammable gases (including chemically unstable gases) (Categories 1 and 2;Categories A and B)
Aerosols (Categories 1,2 and 3)
Oxidising gases (Category 1)
Gases under pressure (Compressed gas, liquefied gas, refrigerated liquefied gas, dissolved gas)
Flammable Liquids (Categories 1,2 and 3)
Flammable solids (Categories 1 and 2)
Self-reactive substance and mixtures (Types A,B,C,D,E,F,G)
Pyrophoric liquids (Category 1)
Pyrophoric solids (Category 1)
Self-heating substances and mixtures (Categories 1 and 2)

Substances and mixtures which in contact water emit flammable gases (Categories 1,2 and 3)
Oxidising liquids (Categories 1,2 and 3)
Oxidising solids (Categories 1,2 and 3)
Organic peroxides (Types A,B,C,D,E,F,G)
Corrosive to metals (Category 1)
HEALTH HAZARDS
Acute toxicity (Categories 1,2,3 and 4)
Skin corrosion /irritation (Categories 1,1A,1B,1C and 2)
Serious eye damage /eye irritation (Categories 1 and 2)
Respiratory or skin sensitisation (Category 1,Sub-categories 1A and 1B)
Germ cell mutagenicity (Categories 1A,1B and 2)
Carcicogenicity (Categories 1A,1B and 2)
Reproductive toxticity (Categories 1A,1B and 2) plus additional category for effect on or via lactation
Specific target organ toxicity (STOT)-single exposure ((Categories 1,2) and Category 3 for narcotic effects and respiratory tract imitation, only)
Specific target organ toxicity (STOT)-repeated exposure (Categories 1 and 2)
Aspiration hazard (Category 1)
ENVIRONMENTAL HAZARDS
Hazardous to the aquatic environmental (Category Acute 1,Category Chronic 1,2,3 and 4)
ADDITIONAL HAZARDS
Hazardous to the ozone layer (Category 1)

A. Physical hazards

According to CLP, the number of hazards classes used to identify physical hazardous substances and mixtures increased from 5 to 16. This does not mean that more materials and mixtures will be classified as dangerous. In most cases, the same substances and mixtures are classified, but we have a more detailed way to identify and identify them.

A.1.Explosives

A.1.1. Definition [1]

Information on the following types of hazards applies to the assessment of substances, mixtures and articles for the explosive class;

- sensitivity to shock;
- effects of heating and ignition under confinement;
- thermal stability;
- sensitiveness to impact and friction;
- mass explosion hazard;
- projection hazard;
- fire and radiant heat hazard.

The classification of explosives according to the GHS is almost entirely adopted based on the UN Recommendations on the Transport of Dangerous Goods.

A.1.2. Criteria for explosives

(a) explosive substances and mixtures;

(b) explosive articles, except devices containing explosive substances or mixtures in such quantity or of such a character that their inadvertent or accidental ignition or initiation shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise; and

(c) substances, mixtures and articles not mentioned in points (a) and (b) which are manufactured with a view to producing a practical, explosive or pyrotechnic effect.

Additional remark related to the applicability of criteria of explosives:

- a substance or mixture which is not itself an explosive but which can form an explosive atmosphere of gas, vapour or dust is not included in this class;

- a substance or mixture with explosive properties, but where the predominant hazard is covered by another class (e.g. organic peroxides, self-reactive substances and mixtures), is not included in the class of explosives.

In addition, the following definitions apply for explosives:

- An explosive substance or mixture is a solid or liquid substance or mixture of substances which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are included even when they do not evolve gases.
- A pyrotechnic substance or mixture is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions.
- An unstable explosive is an explosive which is thermally unstable and/or too sensitive for normal handling, transport and use.
- An explosive article is an article containing one or more explosive substances or mixtures.
- A pyrotechnic article is an article containing one or more pyrotechnic substances or mixtures.
- An intentional explosive is a substance, mixture or article which is manufactured with a view to produce a practical explosive or pyrotechnic effect.

Mixtures and hazardous substances not classified as an unstable explosive will be assigned to one of the following six divisions, depending on their hazard;

(a) Division 1.1 Substances, mixtures and articles which have a mass explosion hazard (a mass explosion is one which affects almost the entire quantity present virtually instantaneously);

(b) Division 1.2 Substances, mixtures and articles which have a projection hazard but not a mass explosion hazard;

(c) Division 1.3 Substances, mixtures and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:

(i) combustion of which gives rise to considerable radiant heat; or

(ii) which burn one after another, producing minor blast or projection effects or both;

(d) Division 1.4 Substances, mixtures and articles which present no significant hazard: substances, mixtures and articles which present only a small hazard in the event of ignition or initiation. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package;

(e) Division 1.5 Very insensitive substances or mixtures which have a mass explosion hazard: substances and mixtures which have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions;

(f) Division 1.6 Extremely insensitive articles which do not have a mass explosion hazard: articles which contain only extremely insensitive substances or mixtures and which demonstrate a negligible probability of accidental initiation or propagation.

The substances, mixtures and articles of this class are classified as unstable explosives based on the flow chart in Figure 2.7. Test methods are described in the UN RTDG, Manual of Tests and Criteria [3].

Figure 2.7. Procedure for provisional acceptance of a substance, mixture or article in the class of explosives (Class 1 for transport).

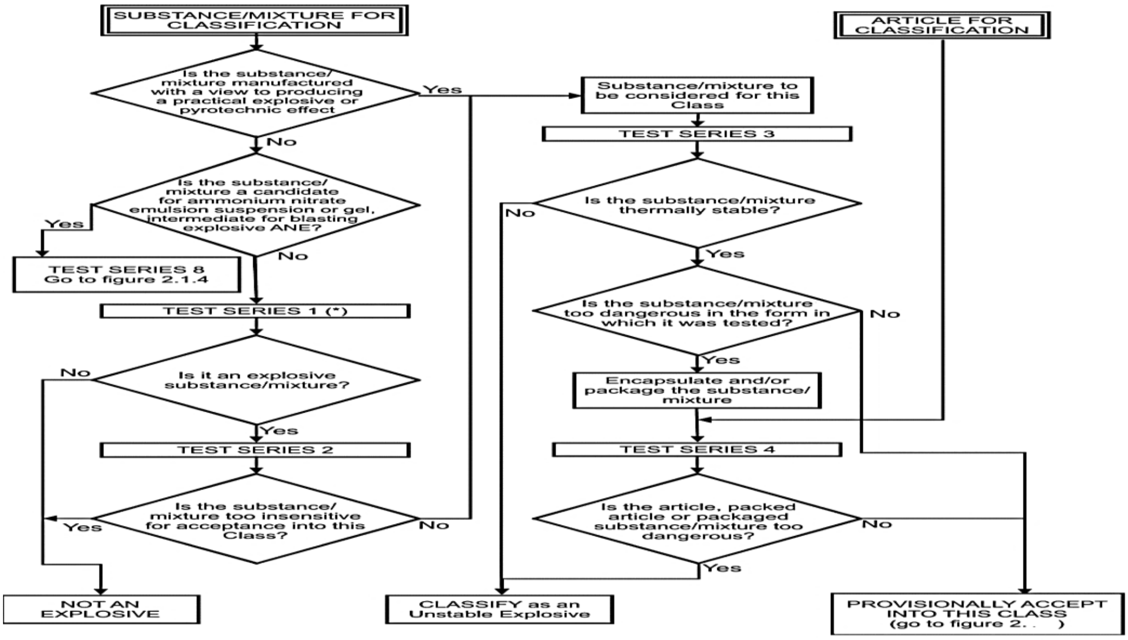


Figure.2.8. Procedure for assignment to a division in the class of explosives.

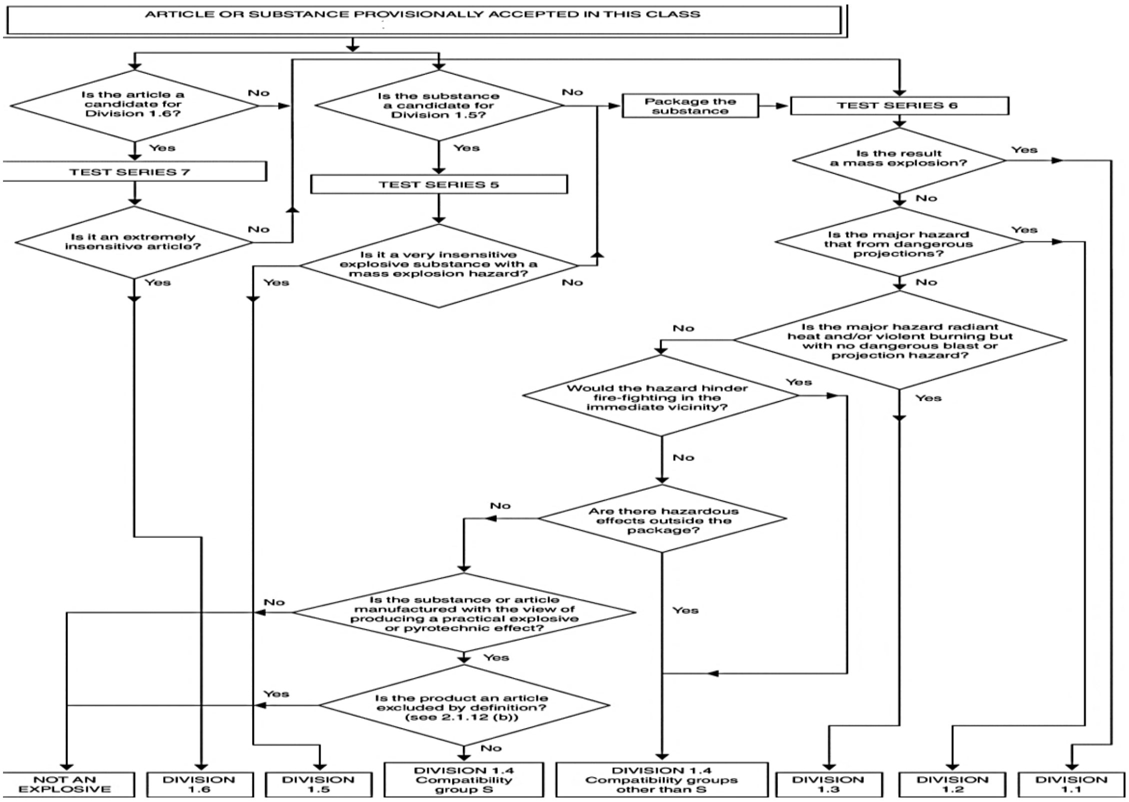


Table.2.9. Pictograms, signal words, hazard statements and precautionary statements for explosives.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Unstable Explosive Division 1.1 Division 1.2 Division 1.3	H200: Unstable Explosive H201: Explosive, mass explosive hazard H202: Explosive, severe projection hazard H203: Explosive, fire, blast or projection	P210 P230 P240 P250 P280	P370+P380 P372 P373 P401	P401	P501

		hazard				
Warming 	Division 1.4	H204: Fire or projection hazard	P210 P240 P25 P280	P370+P380 P372 P373 P401	P401	P501
-	Division 1.5	H205:May mass explode in fire	P210 P230 P240 P250 P280	P370+P380 P372 P373 P401	P401	P501
No pictogram or signal word	Division 1.6	None	No precautionary statement	No precautionary statement	No precautionary statement	Noprecautionary statement

NOTE: Unpackaged explosives or explosives repackaged in packaging other than the original or similar packaging shall include the following label elements:

(a) the pictogram: exploding bomb;

(b) the signal word: “Danger”; and

(c) the hazard statement: 'explosive; mass explosion hazard'

unless the hazard is shown to correspond to one of the hazard categories in Table Labelling of Explosives, in which case the corresponding symbol, signal word and/or the hazard statement shall be assigned.

A.2. Flammable gases

A.2.1. Definition

Flammable gas means a gas or gas mixture having a flammable range with air at 20°C and a standard pressure of 101,3 kPa [1].

A chemically unstable gas means a flammable gas that is able to react explosively even in the absence of air or oxygen.

The flammable range of a flammable gas is defined between the ‘lower explosion (flammability) limit’ (LEL) in air and the ‘upper explosion (flammability) limit’ (UEL) in air.

A.2.2. Criteria for flammable gases

A.2.2.1. Category 1

Gases, which at 20°C and a standard pressure of 101,3 kPa:

(a) are ignitable when in a mixture of 13% or less by volume in air; or

(b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.

A.2.2.2. Category 2

Gases, other than those of Category 1, which, at 20 °C and a standard pressure of 101,3 kPa, have a flammable range while mixed in air.

Many gases are classified as flammable gases in Annex VI of CLP and more gases are classified as flammable gases in the UN RTDG Model Regulations [3].

For gases that are not classified as flammable gases in CLP nor in the UN RTDG Model Regulations, there is ample scientific literature giving the flammability range for most gases (e.g. IEC 60079-20-1, Explosive atmospheres – Part 20-1: Material characteristics for gas and vapour classification – Test methods and data) [4].

Figure.2.10. Decision for flammable gas.

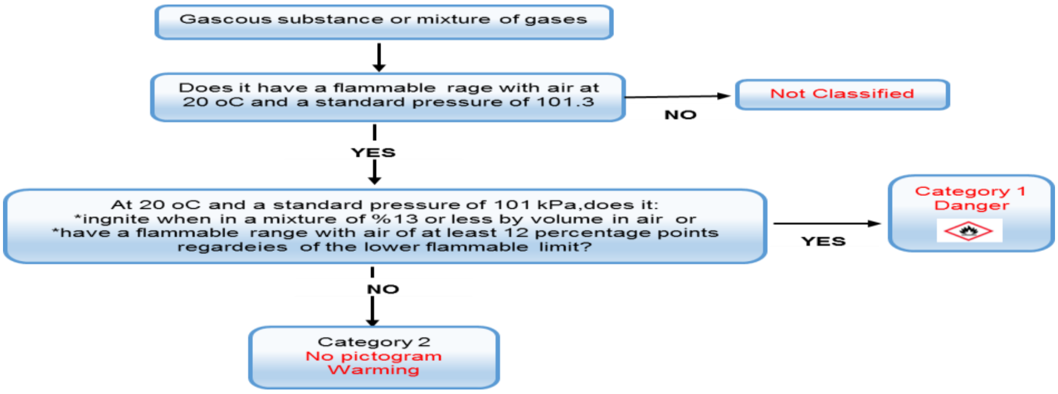


Table.2.9. Pictograms, signal words, hazard statements and precautionary statements for flammable gases.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Flammable gas Category 1	H200: Unstable Explosive H201: Explosive, mass explosive hazard H202: Explosive,severe projection hazard H203: Explosive,fire,blast or projection hazard	P210	P377 P381	P403	-
Warming -	Flammable gas Category 2	H204: Fire or projection hazard	P210	P377 P381	P403	-

A.3. Aerosol

A.3.1. Definition

Aerosols, this means aerosol dispensers, are any non-refillable receptacles made of metal, glass or plastics and containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in a gas, as a foam, paste or powder or in a liquid state or in a gaseous state. (Annex I, Section 2.3 of CLP, Chapter 2.3 of GHS [1] as well as in the Aerosol Dispensers Directive (ADD) 75/324/EEC [5].

A.3.2. Criteria for flammable aerosols

Aerosols shall be considered for classification as flammable if they contain any component which is classified as flammable according to the following criteria set out in this Part:

– Liquids with a flash point ≤ 93 °C, which includes Flammable Liquids;

– Flammable gases;

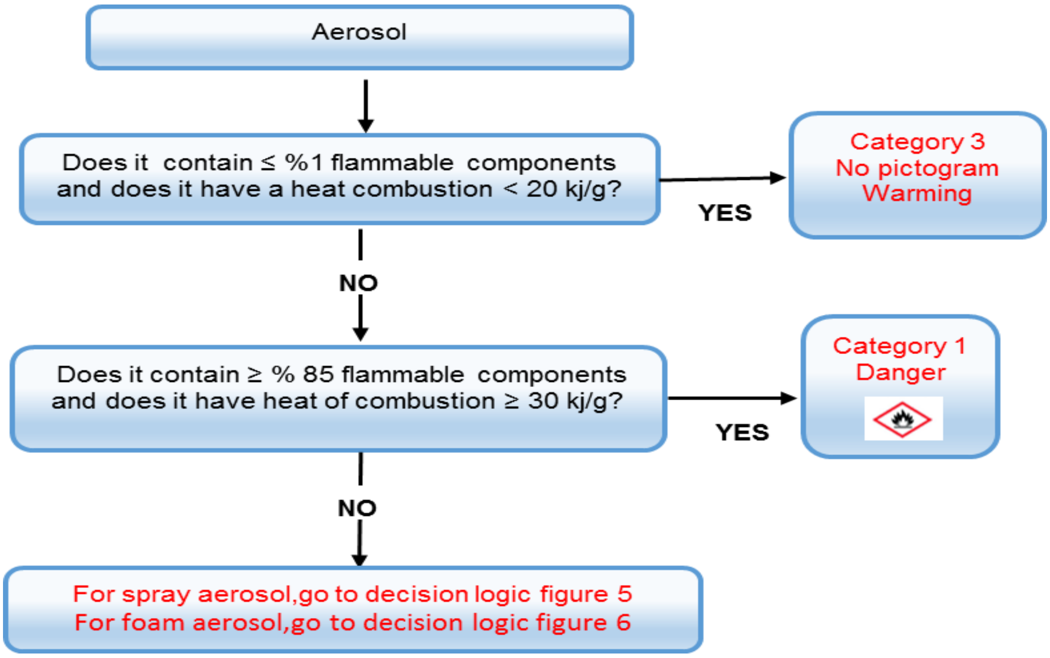
– Flammable solids.

Note 1 [1]:

Flammable components do not cover pyrophoric, self-heating or water-reactive substances and mixtures because such components are never used as aerosol contents.

- An aerosol shall be classified in one of the three categories for this Class on the basis of its components, of its chemical heat of combustion and, if applicable, of the results of the foam test (for foam aerosols) and of the ignition distance test and enclosed space test (for spray aerosols) in accordance with Figures 10 to 12 of this Annex and sub-sections 31.4, 31.5 and 31.6 of Part III of the UN RTDG, Manual of Tests and Criteria [3].
- Aerosols which do not meet the criteria for inclusion in Category 1 or Category 2 shall be classified in Category 3.

Figure.2.11. Decision for flammable aerosols.



Fiqure.2.12. Decision for spray aerosols.

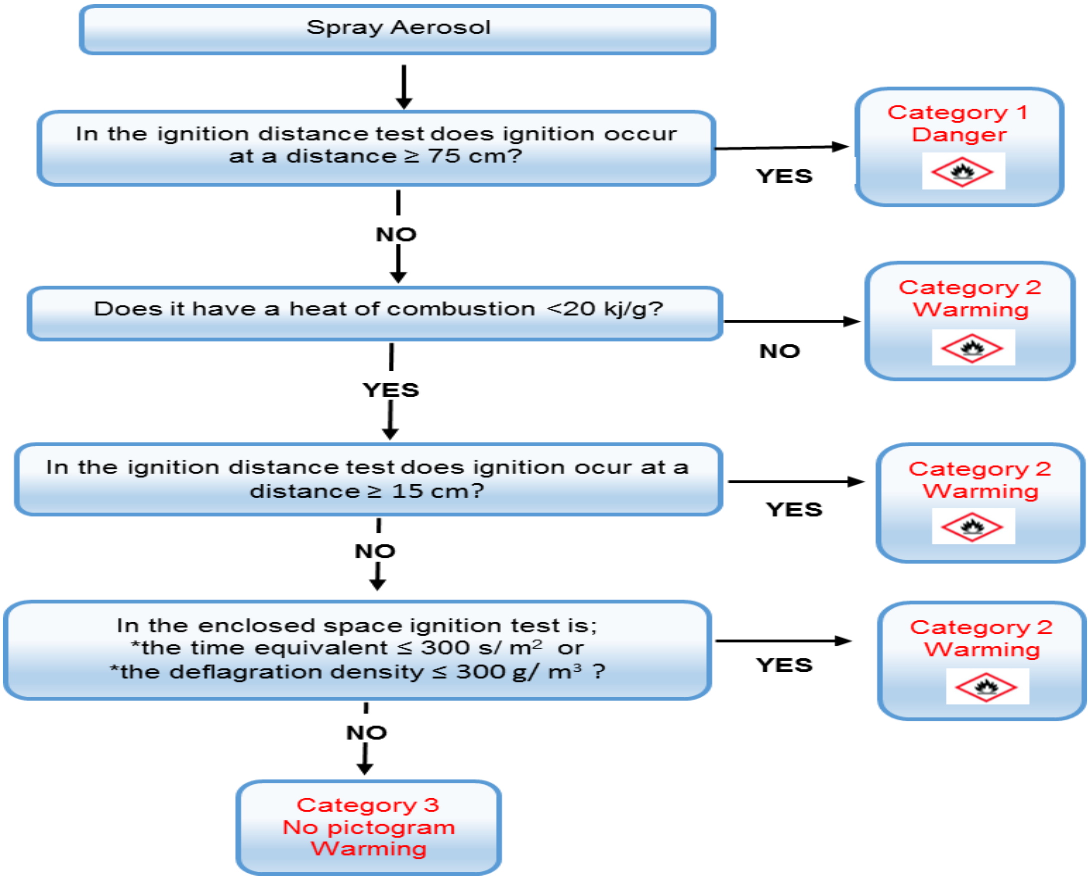


Figure.2.13. Decision for foam aerosols.

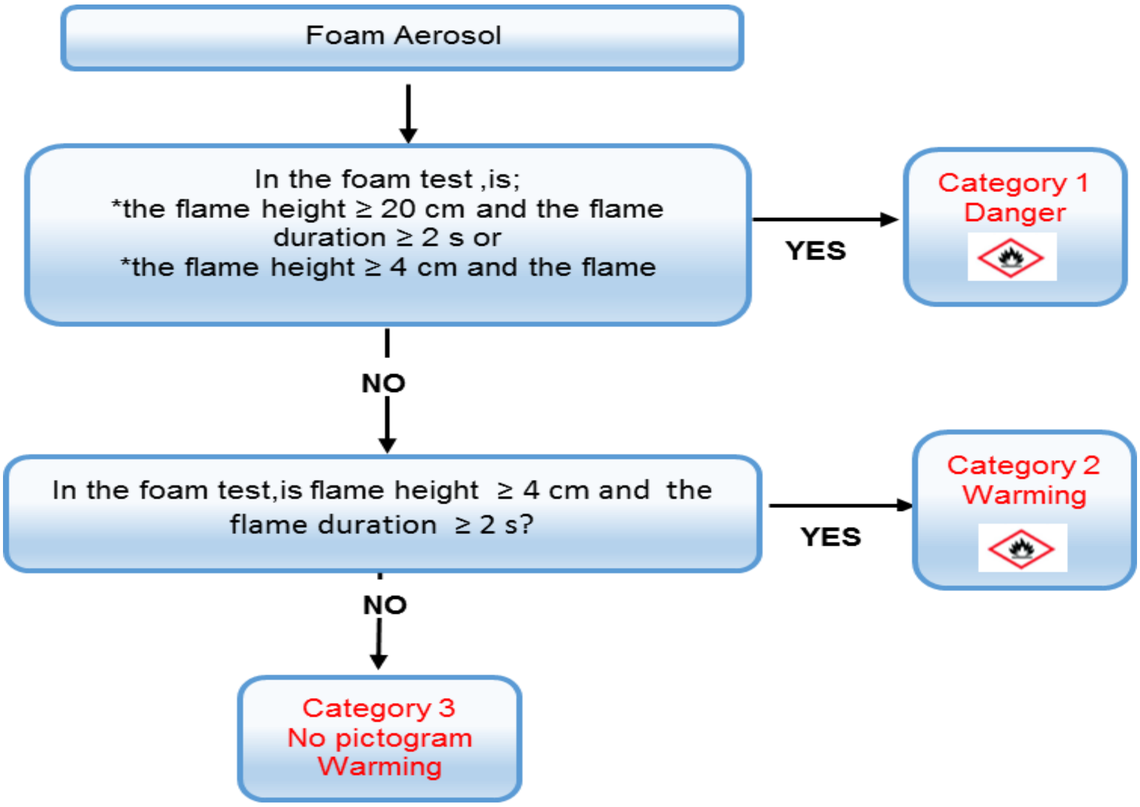


Table.2.10. Pictograms, signal words, hazard statements and precautionary statements for aerosols.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Flammable aerosols Category 1	H222: Extremely flammable aerosol H229: Pressurised container: May burst if heated	P210 P211 P251	-	P410 + P412	-
Warming 	Flammable aerosols Category 2	H223: Flammable aerosol H229: Pressurised container: May burst if heated	P210 P211 P251	-	P410 + P412	-
Warming -	Flammable aerosols Category 3	H229: Pressurised container: May burst if heated	P210 P251	-	P410 + P412	-

A.4. Oxidising gases

A.4.1. Definition

Oxidising gas means any gas or gas mixture which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.

Gases which cause or contribute to the combustion of other material more than air does’ means pure gases or gas mixtures with an oxidising power greater than 23,5 % as determined by a method specified in ISO 10156 [6] as amended.

Fiqure.2.14. Decision for oxidising gases.

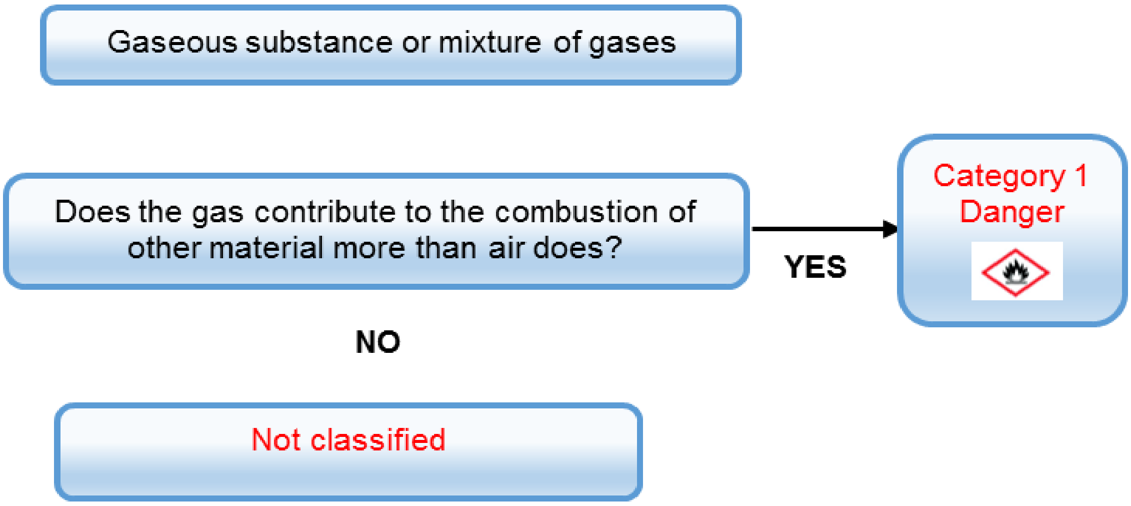


Table.2.11. Pictograms, signal words, hazard statements and precautionary statements for Oxidising Gases.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary StatementResponse**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	oxidising Gas Category 1	H270: May cause or intensify fire, oxider	P220 P244	P370 + P376	P403	-

A.5. Gases under pressure

A.5.1. Definition

- Gases contains; pure gases, mixtures of gases, gases or gas mixtures which contains one or more substances and articles.
- Gas;

i) is a substance which has a vapour pressure greater than 300 kPa (Absolute) at 50˚C or,

ii) is a substance; at the standard pressure 101.3 kPa and at 20˚C is completely gaseous phase.

This definition means that substances and mixtures are considered as gaseous when the boiling point or the first boiling point (BP) is not higher than 20°C.

Substances and mixtures with a boiling point or initial boiling point higher than 20°C are liquids except those few that develop a vapour pressure higher than 300 kPa at 50°C; these substances and mixtures are considered as gases because of the pressure hazard when packaged.

Gases under pressure are gases or gas mixtures which are contained in a receptacle at a pressure of 200 kPa (gauge) or more at 20°C, or which are liquefied or liquefied and refrigerated. These gases classified as a compressed gas, liquefied gases, dissolved gases and refrigerated liquefied gases [1].

So, in practice that compressed gases or dissolved gases that are packaged at a pressure less than 200 kPa are not classified for this hazard

Dissolved gases packaged at a pressure less than 200 kPa (gauge) are liquids and should be classified as such if they have other hazardous properties, e.g. flammable liquids.

The gas can be classified as a ‘compressed gas’, a ‘liquefied gas’, a ‘refrigerated liquefied gas’ and a ‘dissolved gas’ according to The UN RTDG Model Regulations [3]. But, it is not listed in The UN RTDG Model Regulations, physical properties (boiling point and vapourpressure at 50^{o}C) of gases are necessary.

A.5.2. Criteria for gas under pressure

A.5.2.1. Compressed gas

A gas which when packaged under pressure is entirely gaseous at (- 50°C); including all gases with a critical temperature ≤ - 50°C.

A.5.2.2. Liquefied gas

A gas which, when packaged under pressure, is partially liquid at temperatures above - 50 °C. A distinction is made between:

a) high pressure liquefied gas: a gas with a critical temperature between - 50°C and + 65°C; and

b) low pressure liquefied gas: a gas with a critical temperature above + 65°C.

A.5.2.3. Refrigerated liquefied gas

A gas which when packaged is made partially liquid because of its low temperature.

A.5.2.4. Dissolved gas

A gas which when packaged under pressure is dissolved in a liquid phase solvent.

NOTE: The critical temperature of pure gases can be found in technical literature.

For gas mixtures, the classification is based on the ‘pseudo-critical temperature’ which can be estimated as the mole weighted average of the components’ critical temperatures.

Pseudo-critical temperature = $\Sigma = \times niTc$ where,

Xi: molar concentration of component

Tc: Critical temperature of component

Fiqure.2.15. Decision for gas under pressure.

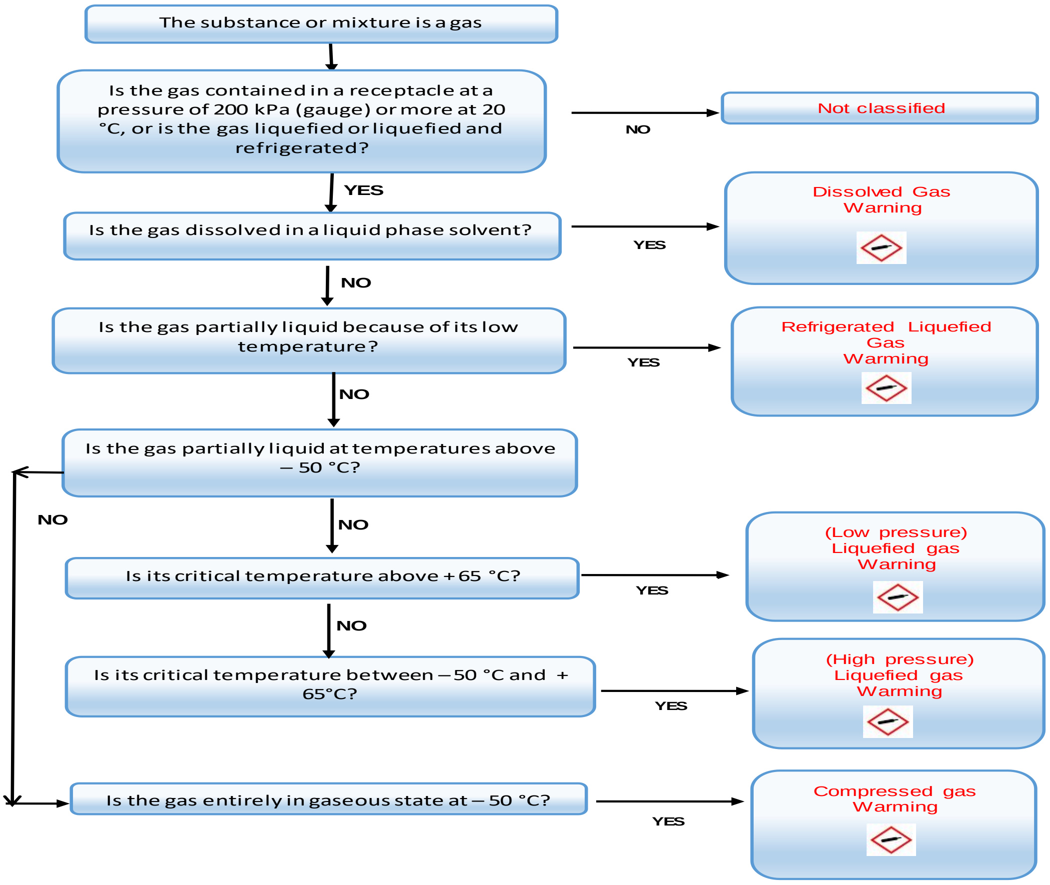


Table.2.12. Pictograms, signal words, hazard statements and precautionary statements for gas under pressure.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement** **Prevention**	**Precautionary Statement** **Response**	**Precautionary Statement** **Storage**	**Precautionary Statement Disposal**
Warming 	Compressed gas Liquefied gas Dissolved gas	H280: Contains gas under pressure, may explode if heated			P410 + P403	-
	Refrigerated Liquefied gas	H281: Contains refrigerated gas, may cause cryogenic burns or injury	P282	P336 P315	P403	-

A.6. Flammable liquids

A.6.1. Definition

Flammable liquid means a liquid having a flash point of not more than 60^{o}C.

A.6.2. Criteria for flammable liquids

A.6.2.1. Category 1

Flash point < 23^{o}C and initial boiling point ≤ 35^{o}C

A.6.2.2. Category 2

Flash point < 23^{o}C and initial boiling point > 35^{o}C

A.6.2.3. Category 3

Flash point ≥ 23^{o}C and ≤ 60^{o}C (1)

(1) For the purpose of this Regulation gas oils, diesel and light heating oils having a flash point between ≥ 55^{o}C and ≤ 75^{o}C may be regarded as Category 3.

Liquids with a flash point of more than 35 °C and not more than 60°C need not be classified in Category 3 if negative results have been obtained in the sustained combustibility test L.2, Part III, section 32 of the UN RTDG, Manual of Tests and Criteria [3].

For the classification of flammable liquids data on flash point and initial boiling point are needed. Data can be determined by testing, found in literature or calculated. If data are not available, the flash point and the initial boiling point shall be determined through testing. For flash point determination a closed-cup method shall be used.

A.6.3. Flash point [7]

The flashpoint of a liquid is the lowest temperature at which the liquid gives off enough vapour to be ignited (start burning) at the surface of the liquid. Sometimes more than one flashpoint is reported for a chemical.,

The following methods for determining the flashpoint of flammable liquids may be used:

International standards:

ISO 1516 :2002	Closed cup equilibrium method
ISO 1523:2002	Closed cup equilibrium method
ISO 2719:2016	Pensky-Martens closed cup method
ISO 13736:2013	Abel closed-cup method
ISO 3679 :2015	Rapid equilibrium closed cup method
ISO 3680:2002	Closed cup equilibrium method

The following methods for determining the initial boiling point of flammable liquids may be used:

International standards:

ISO 3924:2016 Gas chromatography method

ISO 4626:1980 Determination of boiling range of organic solvents used as raw materials

ISO 3405:2011 Determination of distillation characteristics at atmospheric pressure

Calculation should work for pure liquids, neglecting impurities, if the vapour pressure curve and lower explosion limit are accurately known. For mixtures, calculation of the flash point is sometimes not reliable and at this time, it is not possible to predict what the accuracy of a calculated value is. Calculation can be used as a screening test for mixtures, and a flash point need not be determined experimentally if the calculated value using the method cited in CLP Annex I, 2.6.4.3 is 5°C greater than the relevant classification criterion (23°C and 60°C, respectively). However, the restrictions outlined in the CLP [1].

Fiqure.2.16. Decision for flammable liquid.

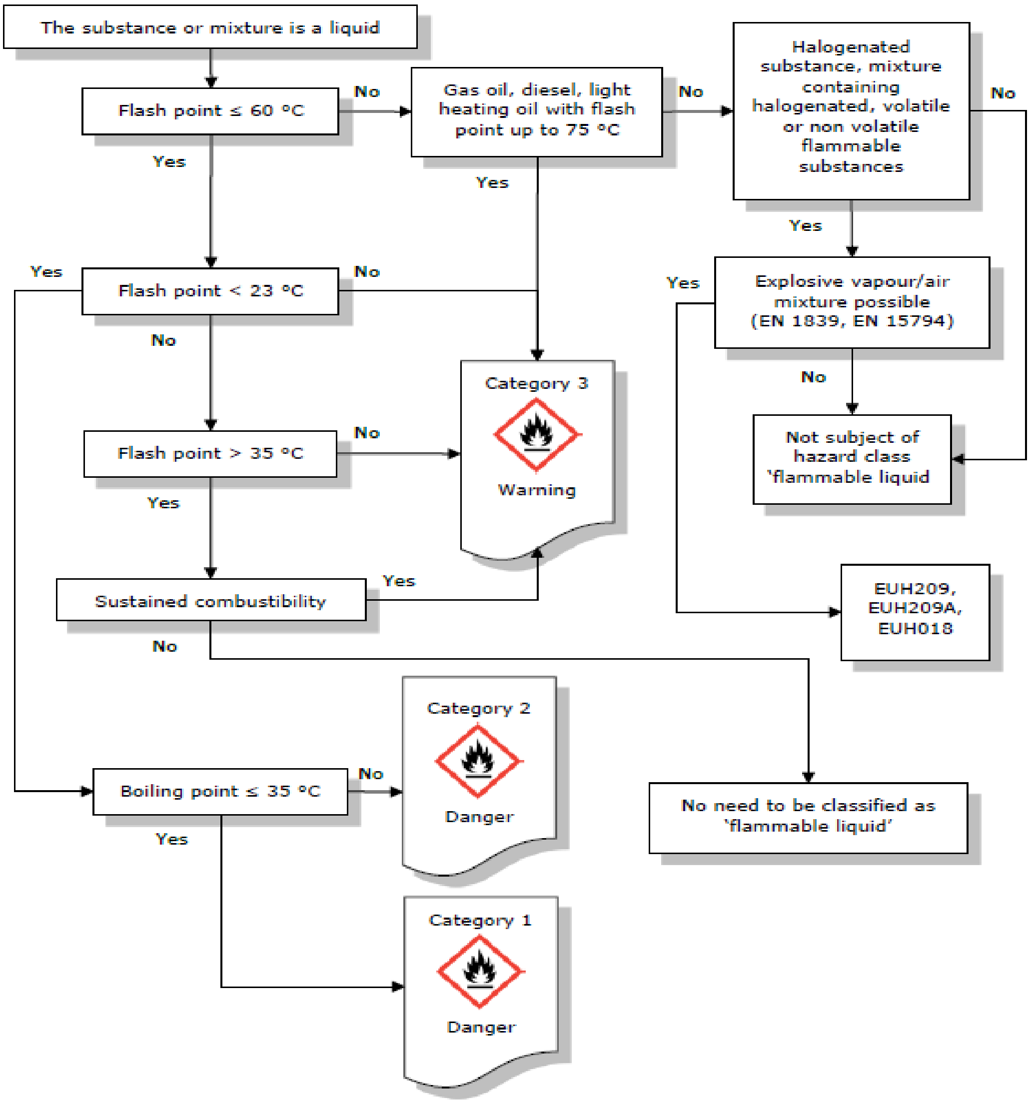


Table.2.13. Pictograms, signal words, hazard statements and precautionary statements for flammable liquids.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal

Danger 	Flammable liquid Category 1	H224: Extremely flammable liquid and vapour	P210, P233, P240, P241, P242,P243,P280	P303 + P361 + P353 P370 + P378	P403 + P235	P501
	Flammable liquid Category 2	H225: Highly flammable liquid and vapour	P210, P233, P240 P241, P242, P243 P280	P303 + P361 + P353 P370 + P378	P403 + P235	P501
Warming 	Flammable aerosols Category 3	H226: Flammable liquid and vapour	P210, P233, P240 P241, P242, P243 P280	P303 + P361 + P353 P370 + P378	P403 + P235	P501

A.7. Flammable solids

A.7.1. Definition

Solids which may cause fire through friction and readily combustible are flammable solids.

Self-reactive solid and liquid substances are thermally unstable substances liable to undergo a strongly exothermic decomposition even without participation of oxygen (air).

These substances are classified to seven according to the degree of danger (A-B-C-D-E-F-G). Type A for example are not accepted for carriage in the packaging in which it is tested, to type G, which is not subject to the provisions for self-reactive substances of Class 4.1. The classification of types B to F is directly related to the maximum quantity allowed in one packaging

Following properties are needed for the classification of the substance or mixture as a flammable solid:

- melting point;

- water reactivity;
- flash point for solids containing flammable liquids.

Powdered, granular or pasty substances or mixtures (except powders of metals or metal alloys) shall be classified as readily combustible solids when the time of burning of one or more of the test runs, performed in accordance with the test method described in Part III, sub-section 33.2.1, of the UN RTDG [3]. Manual of Tests and Criteria, is less than 45 seconds or the rate of burning is more than 2,2 mm/s.

Powders of metals or metal alloys shall be classified as flammable solids when they can be ignited and the reaction spreads over the whole length of the sample in 10 minutes or less.

A possible classification as a flammable solid should be considered for any solid organic substance or mixture containing such material. For inorganic material, if the substance is known as not flammable, testing may be waived. (i.e. stable salts or metal oxides).

Use one of the two categories for this class using Method N.1 as described in 33.2.1 of the UN RTDG [3].

A.7.2. Criteria

A.7.2.1. Category 1

Burning rate test

Substances and mixtures other than metal powders:

(a) wetted zone does not stop fire and

(b) burning time < 45 seconds or burning rate > 2,2 mm/s

Metal powders:

burning time ≤ 5 minutes

A.7.2.2. Category 2

Burning rate test

Substances and mixtures other than metal powders:

(a) wetted zone stops the fire for at least 4 minutes and

(b) burning time < 45 seconds or burning rate > 2,2 mm/s

Metal powders:

burning time > 5 minutes and ≤ 10 minutes

<u>Note:</u> Aerosols shall not be classified as flammable solids.

Fiqure.2.17. Decision for flammable solids.

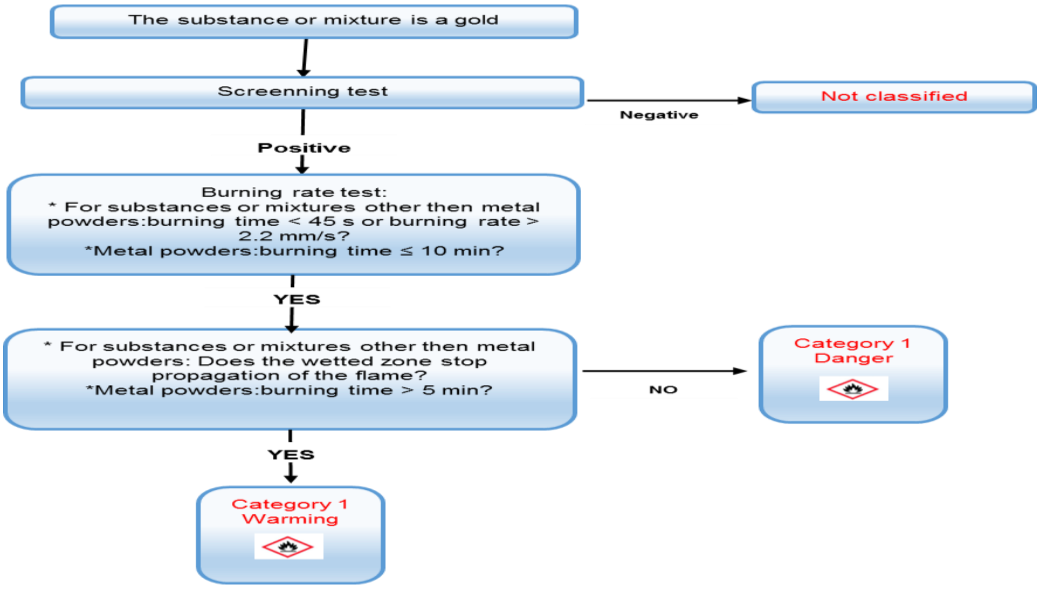


Table.2.14. Pictograms, signal words, hazard statements and precautionary statements for flammable solids.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statemen** **Prevention**	**Precautionary Statement** **Response**	**Precautionary Statement** **Storage**	**Precautionary Statement Disposal**
Danger 	Flammable solid Category 1	H228: Flammable solid	P210 P240 P241 P280	P370 + P378	-	-
Warming 	Flammable solid Category 2		P210 P240 P241 P280	P370 + P378	-	-

By using a diluent, self-reactive substances are desensitized during transportation. But, the substance shall be tested with the diluent and in the form of carriage. Diluents shall be compatible with the self-reacting substance. Diluents that allow a self-reactive substance to concentrate to a dangerous extent in an event of leakage shall not be used.

A.8. Self-reactive substances and mixtures

A.8.1. Definition

Self-reactive substances or mixtures are thermally unstable liquid or solid substances or mixtures liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes substances and mixtures classified according to this Part as explosives, organic peroxides or as oxidising.

A self-reactive substance or mixture possess explosive properties in laboratory testing, can detonate, deflagrate rapidly or shows violent effect when heated under closed containers

Self-reactive substances and mixtures shall be classified in one of the seven categories of ‘types A to G’ for this class, according to the following principles [1]:

(a) substance/mixture detonates or deflagrates rapidly, as packaged, is defined as self-reactive substance TYPE A;

(b) substance/mixture possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package shall be defined as self-reactive substance TYPE B;

(c) substance/mixture possessing explosive properties when the substance or mixture as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion shall be defined as self-reactive substance TYPE C;

(d) substance/mixture which in laboratory testing:

(i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or

(ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or

(iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement;

Is defined as TYPE D;

(e) substance/mixture, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement shall be defined as self-reactive substance TYPE E;

(f) substance/mixture, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power shall be defined as self-reactive substance TYPE F;

(g) substance/mixture, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable (SADT is 60^{o}C to 75^{o}C for a 50 kg package), and, for liquid mixtures, a diluent having a boiling point not less than 150^{o}C is used for desensitisation shall be defined as self-reactive substance TYPE G. If the mixture is not thermally stable or a diluent having a boiling point less than 150^{o}C is used for desensitisation, the mixture shall be defined as self-reactive substance TYPE F.

If the substance is carried with a package, changing the packaging will affect the outcome of the test, that will require a further test.

A.8.2. Temperature control criteria

The SADT is defined as the lowest temperature at which self-accelerating decomposition of a substance or mixture may occur in the packaging as used in transport, handling and storage. The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the substance or mixture and its packaging

The SADT is used to derive safe handling, storage and transport temperatures (control temperature) and alarm temperature (emergency temperature).

Depending on its SADT a self-reactive substance and mixture needs temperature control and the rules as given in CLP [1].

1. Criteria for temperature control:

2. Self-reactive substances and mixtures need to be subjected to temperature control when the SADT is ≤ 55°C.

3. Derivation of control and emergency temperatures.

Fiqure.2.18. Decision for self-reactive substances and mixtures.

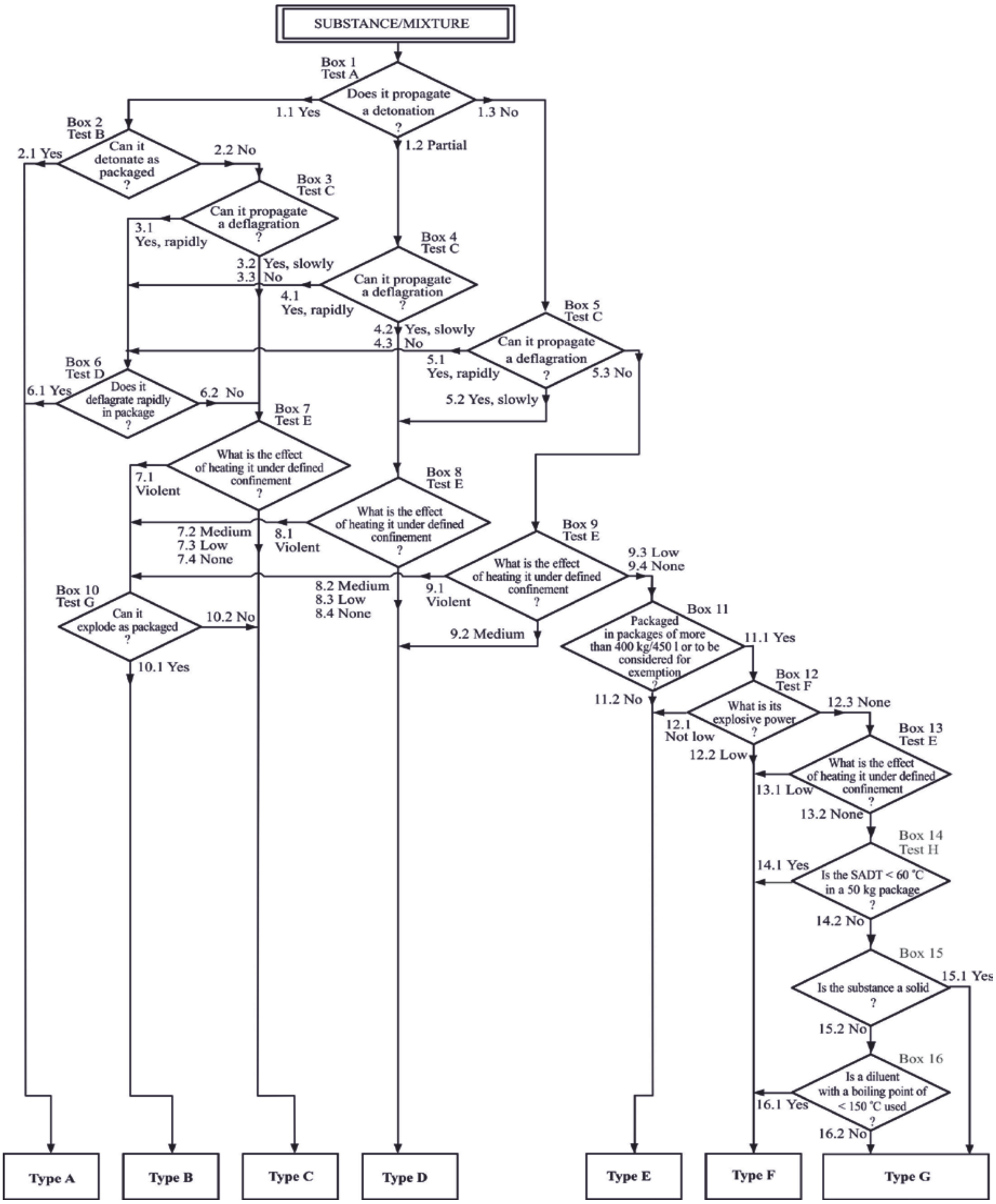


Table.2.15. Pictograms, signal words, hazard statements and precautionary statements for self-reactive substances and mixture.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal

Danger 	Self – reactive substances Type A	H240: Heating may cause an explosion	P210 P220 P234 P280	P370 + P378 P370 + P380 + P375	P403 + P235 P411 P420	P501
Danger 	Self – reactive substances Type B	H241: Heating may cause a fire or explosion	P210 P220 P234 P280	P370 + P378 P370 + P380 + P375	P403 + P235 P411 P420	P501
Danger 	Self – reactive substances Types C&D	H242: Heating may cause a fire	P210 P220 P234 P280	P370 + P378	P403 + P235 P411 P420	P501
Warming 	Self – reactive substances Types E&F	H242: Heating may cause a fire	P210 P220 P234 P280	P370 + P378	P403 + P235 P411 P420	P501
-	Self – reactive substances Type G	-				

A.9. Pyrophoric liquids and solids

A.9.1. Definition

If a liquid material even in small quantities is able to ignite in five minutes after exposure to air, it is called a Pyrophoric liquid.

A.9.2. Criteria

A.9.2.1. Pyrophoric liquids

The liquid ignites within 5 min when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 min (Category 1).

A.9.2.2. Pyrophoric solids

The solid ignites within 5 minutes of coming into contact with air (Category 1).

Table.2.16. Pictograms, signal words, hazard statements and precautionary statements for pyrophoric liquids and solids.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement** **Prevention**	**Precautionary Statement** **Response**	**Precautionary Statement** **Storage**	**Precautionary Statement Disposal**
Danger 	Pyrophoric liquids Category 1	H250: Catches fire spontaneously if exposed to air	P210 P222 P280	P302 + P334	P370 + P378	P422
	Pyrophoric solids Category 1		P210 P222 P280	P335 + P334	P370 +P378	P422

A.10. Self-heating substances and mixtures

A.10.1. Definition

Other than the pyrophoric substances a substance/mixture by reaction with air without energy supply, is liable to self-heat; that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days).

Self-heating of a substance or a mixture is a process where the gradual reaction of that substance or mixture with oxygen (in the air) generates heat. If the rate of heat production exceeds the rate of heat loss, then the temperature of the substance or mixture will rise which, after an induction time, may lead to self-ignition and combustion.

A.10.2. Criteria

A self-heating substance/mixture is classified in one of the two categories for this class if, in a test performed in accordance with UN Test N.4 in Part III, Sub-section 33.3.1.6 of the UN-RTG [3], the result meets the criteria according to following table.

Substances and mixtures with a temperature of spontaneous combustion higher than 50 °C for a volume of 27 m^3 shall not be classified as a self-heating substance or mixture.

Substances and mixtures with a spontaneous ignition temperature higher than 50 °C for a volume of 450 litres shall not be assigned to Category 1 of this class.

A.10.2.1. Category 1

A positive result is obtained in a test using a 25 mm sample cube at 140°C

A.10.2.2. Category 2

(a) a positive result is obtained in a test using a 100 mm sample cube at 140^{0}C and a negative result is obtained in a test using a 25 mm cube sample at 140^{0}C and the substance or mixture is to be packed in packages with a volumeof more than 3 m3; or

(b) a positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a positive result is obtained in a test using a 100 mm cube sample at 120°C and the substance or mixture is to be packed in packages with a volume of more than 450 litres; or;

(c) a positive result is obtained in a test using a 100 mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and a positive result is obtained in a test using a 100 mm cube sample at 100°C.

Note: The test shall be performed on the substance or mixture in its physical form as presented. If, for example, for the purposes of supply or transport, the same chemical is to be presented in a physical form different from that which was tested and which is considered likely to materially alter its performance in a classification test, the substance shall also be tested in the new form.

Fiqure.2.19. Decision for Self-Heating Substances and Mixtures.

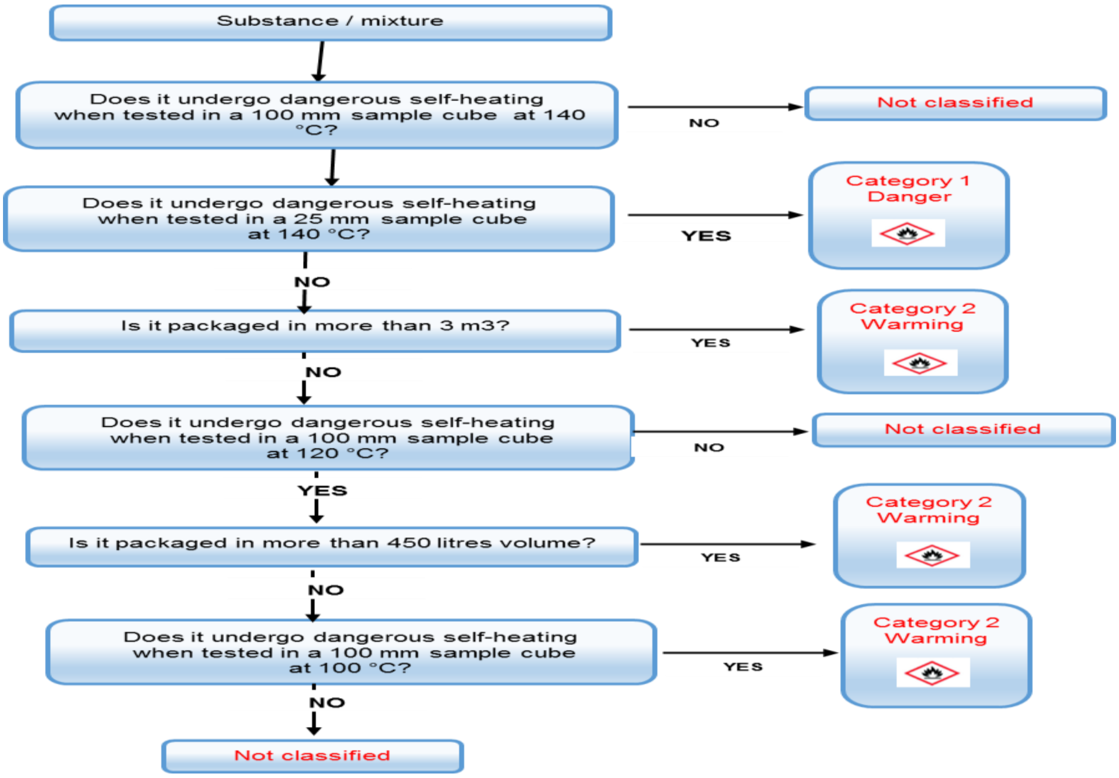


Table.2.17. Pictograms, signal words, hazard statements and precautionary statements for self-heating substances and mixture.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement** **Prevention**	**Precautionary Statement** **Response**	**Precautionary Statement** **Storage**	**Precautionary Statements Disposal**
Danger 	Category 1	H251: Self-heating; may catch fire.	P235 + P410 P280	-	P407 P413 P420	-
Warming 	Category 2	H252: Self-heating in large quantities; may catch fire.	P235 + P410 P280	-	P407 P413 P420	-

A. 11. Substances and mixtures which in contact with water, emit flammable gases

A.11.1. Definition

Substances or mixtures which, in contact with water, emit flammable gases means solid or liquid substances or mixtures which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

A.11.1. Criteria

A.11.1.1. Category 1

Any substance or mixture which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.

A.11.1.2. Category 2

Any substance or mixture which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Category 1.

A.11.1.3. Category 3

Any substance or mixture which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Categories 1 and 2.

Table.2.18. Pictograms, signal words, hazard statements and precautionary statements.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal

Danger 	Water reactive Category 1	H260: In contact with water releases flammable gases which may ignite spontaneously	P223 P231 + P232 P280	P335 + P334 P370 + P378	P402 + P404	P501
Danger 	Water reactive Category 2	H261: In contact with water releases flammable gases	P223 P231 + P232 P280	P335 + P334 P370 + P378	P402 + P404	P501
Warming 	Water reactive Category 3		P231 + P232 P280	P370 + P378	P402 + P404	P501

A.12. Oxidising liquids and solids

A.12.1. Definition

Oxidising liquid means a liquid substance or mixture which, while in itself not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

Oxidising solid means a solid substance or mixture which, while in itself is not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material.

A.12.1. Criteria

A.12.1.1. Category 1

Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of substance (or mixture) and cellulose is less than that of a 1:1 mixture, by mass, of 50 % per chloric acid and cellulose.

A.12.1.2. Category 2

Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40 % aqueous sodium chlorate solution and cellulose; and the criteria for Category 1 are not met.

A.12.2.1. Category 3

Any substance or mixture which, in the 1:1 mixture, by mass, of substance (or mixture) and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65 % aqueous nitric acid and cellulose; and the criteria for Category 1 and 2 are not met.

Table.2.19. Pictograms, signal words, hazard statements and precautionary statements for oxidising liquids and solids.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Oxidising liquid Category 1 Oxidising solid Category 1	H271: May cause fire or explosion, strong oxidiser	P210 P220 P221 P280 P283	P306 + P360 P371 + P380 + P375 P370 + P378	-	P501
Danger 	Oxidising liquid Category 2 Oxidising solid Category 2	H272: May intensity fire, oxidiser	P210 P220 P221 P280	P370 + P378	-	P501
Warming 	Oxidising liquid Category 3 Oxidising solid Category 3		P210 P220 P221 P280	P370 + P378	-	P501

A. 13. Organic peroxides

A.13.1. Definition

Organic peroxides mean liquid or solid organic substances which contain the bivalent -O-O- structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. The term organic peroxide includes organic peroxide mixtures (formulations) containing at least one organic peroxide. Organic peroxides are thermally unstable substances or mixtures, which can undergo exothermic self-accelerating decomposition. In addition, they can have one or more of the following properties:

be liable to explosive decomposition;

burn rapidly;

be sensitive to impact or friction;

react dangerously with other substances.

An organic peroxide is regarded as possessing explosive properties when in laboratory testing the mixture (formulation) is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

Any organic peroxide shall be considered for classification in this class, unless it contains:

(a) not more than 1,0 % available oxygen from the organic peroxides when containing not more than 1,0 % hydrogen peroxide; or

(b) not more than 0,5 % available oxygen from the organic peroxides when containing more than 1,0 % but not more than 7,0 % hydrogen peroxide.

The available oxygen content (%) of an organic peroxide mixture is given by the formula:

$$16 \times \sum_{i}^{n} \left(\frac{n_i \times n_j}{m_i} \right)$$

Where:

ni= number of per oxygen groups per molecule of organic peroxide i;

ci= concentration (mass %) of organic peroxide i;

$m_{i=}$ molecular mass of organic peroxide i.

Organic peroxides shall be classified in one of the seven categories of ‘Types A to G’ for this class, according to the following principles:

(a) any organic peroxide which, as packaged, can detonate or deflagrate rapidly shall be defined as organic peroxide TYPE A;

(b) any organic peroxide possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package shall be defined as organic peroxide TYPE B;

(c) any organic peroxide possessing explosive properties when the substance or mixture as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion shall be defined as organic peroxide TYPE C;

(d) any organic peroxide which in laboratory testing:

(i) detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or

(ii) does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or

(iii) does not detonate or deflagrate at all and shows a medium effect when heated under confinement; shall be defined as organic peroxide TYPE D;

(e) any organic peroxide which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement shall be defined as organic peroxide TYPE E;

(f) any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power shall be defined as organic peroxide TYPE F;

(g) any organic peroxide which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power, provided that it is thermally stable, i.e. the SADT is 60 oC or higher for a 50 kg package (8), and, for liquid mixtures, a diluent having a boiling point of not less than 150^{o}C is used for desensitisation, shall be defined as organic peroxide

TYPE G. If the organic peroxide is not thermally stable or a diluent having a boiling point less than 150°C is used for desensitisation, the organic peroxide shall be defined as organic peroxide TYPE F.

Where the test is conducted in the package form and the packaging is changed, a further test shall be conducted where it is considered that the change in packaging will affect the outcome of the test.

Temperature Control;

The following organic peroxides need to be subjected to temperature control:

a. Organic peroxide types B and C with a SADT ≤ 50°C;

b. Organic peroxide type D showing a medium effect when heated under confinement with a SADT ≤ 50°C or showing a low or no effect when heated under confinement with a SADT ≤ 45°C; and

c. Organic peroxide types E and F with a SADT ≤ 4°C.

For the determination of the SADT, the testing method in UN-MTC, Part II, Section 28, may be used.

Figure.2.20. Decision for oxidising peroxide.

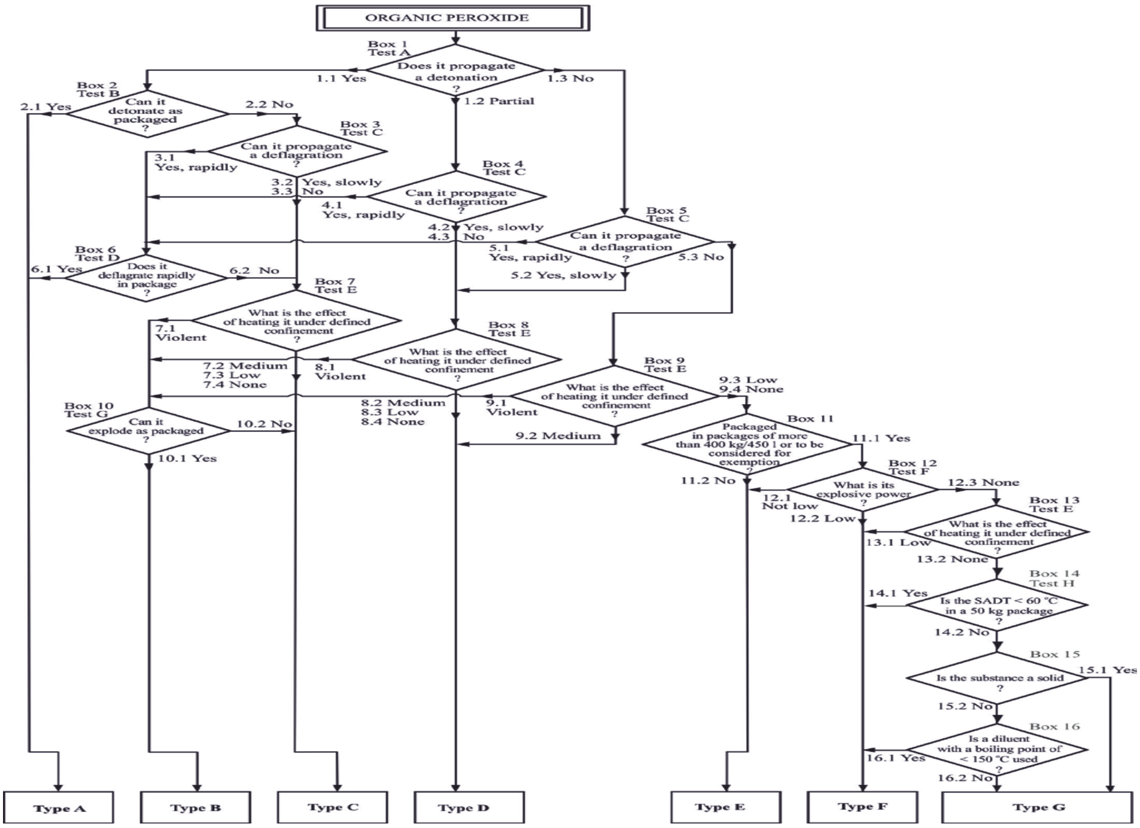


Table.2.20. Pictograms, signal words, hazard statements and precautionary statements for organic peroxides.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Organic peroxide Type A	H240: Heating may cause an explosion	P210 P220 P234 P280	-	P411 + P235 P410 P420	P501
Danger 	Organic peroxide Type B	H241: Heating may cause a fire or explosion	P210 P220 P234 P280	-	P411 + P235 P410 P420	P501
Danger 	Organic peroxide Types C&D	H242: Heating may cause a fir	P210 P220 P234 P280	-	P411 + P235 P410 P420	P501
Warming 	Organic peroxide Types E&F	H242: Heating may cause a fire	P210 P220 P234 P280	-	P411 + P235 P410 P420	P501
-	Organic peroxide Type G	-				

A. 14. Corrosive to metals

A.14.1. Definition

A substance or a mixture that is corrosive to metals means a substance or a mixture which by chemical action will materially damage, or even destroy, metals.

A.14.2. Criteria

Corrosion rate on either steel or aluminium surfaces exceeding 6,25 mm per year at a test temperature of 55°C when tested on both materials (Category 1).

Where an initial test on either steel or aluminium indicates the substance or mixture being tested is corrosive, the follow up test on the other metal is not required.

Table.2.21. Pictograms, signal words, hazard statements and precautionary statements for corrosive to metals.

CLP pictogram and signal word	**Hazard Class and Category**	**Hazard Statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Warming 	Metal corrosive Category 1	H290: May be corrosive to metals	P234	P390	P406	-

B. Health hazards

B.1. Acute toxicity

B.1.1. Definition

Acute toxicity describes the adverse effects of a substance that result either from a single exposure or from multiple exposures in a short period of time (usually less than 24 hours).[8] To be described as acute toxicity, the adverse effects should occur within 14 days of the administration of the substance [9].

Acute toxicity classification is generally assigned on the basis of evident lethality (e.g. an LD50/LC50 value),

LD50; LD stands for "Lethal Dose". LD50 is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD50 is one way to measure the short-term poisoning potential (acute toxicity) of a material.

LC50; LC stands for "Lethal Concentration". LC values usually refer to the concentration of a chemical in air but in environmental studies it can also mean the concentration of a chemical in water. The concentrations of the chemical in air that kills 50% of the test animals during the observation period is the LC50 value.

The hazard class Acute Toxicity is differentiated into:

Acute oral toxicity;

Acute dermal toxicity;

Acute inhalation toxicity.

Substances can be assigned to one of four toxicity categories based on acute toxicity by the oral, dermal or inhalation according to the numeric criteria [1].

Table.2.22. Acute toxicity hazard categories and acute toxicity estimates (ATE) defining the respective categories.

Exposure route	**Category 1**	**Category 2**	**Category 3**	**Category 4**
Oral (mg/kg bodyweight)	ATE ≤ 5	5 < ATE ≤ 50	50 < ATE ≤ 300	300 < ATE ≤ 2 000
Dermal (mg/kg bodyweight)	ATE ≤ 50	50 < ATE ≤ 200	200 < ATE ≤ 1 000	1 000 < ATE ≤ 2 000
Gases (ppmV)	ATE ≤ 100	100 < ATE ≤ 500	500 < ATE ≤ 2 500	2 500 < ATE ≤ 20 000
Vapours (mg/l)	ATE ≤ 0,5	0,5 < ATE ≤ 2,0	2,0 < ATE ≤ 10,0	10,0 < ATE ≤ 20,0
Dusts and mists (mg/l)	ATE ≤ 0,05	0,05 < ATE ≤ 0,5	0,5 < ATE ≤ 1,0	1,0 < ATE ≤ 5,0

Notes:

(a) The acute toxicity estimate (ATE) of a substance or a mixture of ingredients is derived using LD50 / LC50 where possible.

(b) The acute toxicity estimate (ATE) of a substance or of a mixture is derived using the following;

- the LD50/LC50 where available,

(c) The ranges of the acute toxicity estimates (ATE) for inhalation toxicity in the table are based on 4-hour testing exposures. Conversion of existing inhalation toxicity data which have been generated using a 1-hour exposure can be carried out by dividing by a factor of 2 for gases and vapours and dividing by a factor of 4 for dusts and mists.

(ç) For some substances or mixtures, the test atmosphere consists of a mixture of liquid and vapour phases, not just this vapour. For other substances and mixtures, the test atmosphere may contain vapour near the gas phase. In these cases, the classification should be based on ppmV, as follows; Category 1 (100 ppmV), Category 2 (500 ppmV), Category 3 (2500 ppmV), Category 4 (20 000 ppmV).

Units for inhalation toxicity are a function of the form of inhaled material. Values for powders and mists are expressed in mg / l and for gases are expressed in ppmV. Since the difficulties of testing vapours, some of which are mixtures of liquid and vapour states, are known, the values in the table are expressed in mg / l. However, the classification of vapours close to the gaseous phase is made taking into account the values in ppm V.

Components of a mixture should be classified in that category if the acute toxicity for all components of a mixture is in the same category.

The ATE of the mixture is determined by calculation from the ATE values for all relevant ingredients according to the following formula for Oral, Dermal or Inhalation Toxicity [1]:

$$\frac{100}{\mathrm{ATE_{mix}}} = \sum_{n} \frac{C_i}{\mathrm{ATE_i}}$$

where:

C_i= concentration of ingredient i (% w/w or % v/v)

i= the individual ingredient from 1 to n

ATE_i = Acute Toxicity Estimate of ingredient i.

When evaluating the available information for the purposes of classification, the manufacturers, importers and downstream users shall consider the forms or physical states in which the substance or mixture is placed on the market and in which it can reasonably be expected to be used

Table.2.23. Pictograms, signal words, hazard statements and precautionary statements for oral acute toxicity.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention(oral)**	**Precautionary Statement Response (oral)**	**Precautionary Statement Storage(oral)**	**Precautionary Statement Disposal(oral)**
Danger 	Acute toxicity Category 1 Acute toxicity Category 2	H300: Fatal ıf swallowed H310: Fatal in contact with skin H330:Fatal if inhaled	P264 P270	P301 + P310 P321 P330	P405	P501
	Acute toxicity Category 3	H301: Toxic if swallowed H311: Toxic in contact with skin H331:Toxic if inhaled	P264 P270	P301 + P310 P321 P330	P405	P501
Warming 	Acute toxicity Category 4	H302: Harmful if swallowed H312: Harmful in contact with skin H332:Hamful if inhaled	P264 P270	P301 + P312 P330	-	P501

Table.2.24. Pictograms, signal words, hazard statements and precautionary statements for dermal acute toxicity.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention (Dermal)**	**Precautionary Statement Response (Dermal)**	**Precautionary Statement Storage (Dermal)**	**Precautionary Statement Disposal (Dermal)**
Danger	Acute toxicity Category 1 Acute	H300: Fatal ıf swallowed H310: Fatal in contact	P262 P264 P270 P280	P302 + P352 P310 P321 P361 + P364	P405	P501

	toxicity Category 2	with skin H330:Fatal if inhaled				
	Acute toxicity Category 3	H301: Toxic if swallowed H311: Toxic in contact with skin H331:Toxic if inhaled	P280	P302 + P352 P310 P321 P361 + P364	P405	P501
Warming 	Acute toxicity Category 4	H302: Harmful if swallowed H312: Harmful in contact with skin H332: Harmful if inhaled	P280	P302 + P352 P310 P321 P361 + P364	-	P501

B.2. Skin corrosion and irritation

B.2.1. Definition

Skin Corrosion means the production of irreversible damage to the skin; namely, visible necrosis through the epidermis and into the dermis, following the application of a test substance for up to 4 hours

Skin Irritation means the production of reversible damage to the skin following the application of a test substance for up to 4 hours.

The corrosive category, for animals, consists of three subcategories: Subcategory 1A - when reactions are recorded for up to 3 minutes and after 1 hour of observation, Subcategory 1B - where responses are defined by observations from 3 minutes to 1 hour after exposure and up to 14 days and the 1C sub-category of responses emerged after observations from 1 hour to 4 hours and up to 14 days.

Table.2.25. Skin corrosive category and subcategories.

	Corrosive subcategories	Corrosive in > 1 of 3 animals	
		Exposure	Observation
Category 1: Corrosive	1A	≤ 3 minutes	≤ 1 hour
	1B	> 3 minutes - ≤ 1 hour	≤ 14 days
	1C	> 1 hour - ≤ 4 hours	≤ 14 days

The following assumptions have been made in order to use all of the available data in order to classify the hazard of the mixtures and this assumption has been applied where appropriate in the gradual approach [1]. Assumption: the "relevant components" of the mixture are of a composition which is present at a concentration of less than 1% (w/w for solids, liquids, dusts, mists and vapours and v/v for gases), unless there is a possibility that the mixture is still relevant for the classification of the skin irritation / corrosion (eg in the case of corrosion components) are present at a concentration of 1% or more.

The approach to classifying mixtures as irritant or corrosive for the skin, when concentration data available into the components, but not as a whole, based on additivity theory, such that each corrosive or irritant component contributes to the overall irritant or corrosive properties of the mixture in proportion to its potency and concentration. Corrosive components below the generic concentration limit for classification with Category 1, weighting factor (10) used. If sum of all such component concentration exceeds the concentration limit, mixture classified as irritant/corrosive for skin.

Table.2.26. Generic concentration limits of ingredients classified for skin corrosive/irritant hazard (category 1 or 2) that trigger classification of the mixture as corrosive/irritant to skin.

	Concentration triggering classification of a mixture as:	
	Skin Corrosive	**Skin Irritant**
	Category 1	**Category 2**

Skin Corrosive Categories 1A, 1B, 1C	≥ 5 %	≥ 1 % but < 5 %
Skin irritant Category 2		≥ 10 %
(10 × Skin Corrosive Category 1A, 1B, 1C) +		≥ 10 %

The sum of all each component in mixture classified as Skin Corrosive Category 1A, 1B or 1C, must be ≥ 5% respectively to classify the mixture as a corrosive category 1A, 1B or 1C for the skin.

If the sum of the Skin Corrosive Category 1A ingredients is < 5 % but the sum of Category 1A+1B ingredients is ≥ 5 %, the mixture shall be classified as Skin Corrosive Category 1B.

Similarly, if the sum of Skin Corrosive Category 1A+1B ingredients is < 5 % but the sum of Category 1A+1B+1C ingredients is ≥ 5 % the mixture shall be classified as Skin Corrosive Category 1C.

The mixture is classified for skin corrosion/irritation if the:

Sum of (AConc / ACL) + (BConc / BCL) + …. + (ZConc / ZCL) is ≥ 1

Where AConc = the concentration of substance A in the mixture;

ACL = the concentration limit (either specific or generic) for substance A;

Where BConc = the concentration of substance B in the mixture;

clB = the concentration limit (either specific or generic) for substance B; etc.

Table.2.27. Pictograms, signal words, hazard statements and precautionary statements for skin corrosive/irritation.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement** **Prevention**	**Precautionary Statement** **Response**	**Precautionary Statement** **Storage**	**Precautionary Statement Disposal**
Danger 	Skin corrosion Category 1A	H314:Causes severe skin burns and eye damage	P260 P264 P280	P301 + P330 + P331 P303 + P361 + P353 P363 P304 + P340	P405	P501
	Skin corrosion					

	Category 1B&1C			P310 P321 P305 + P351 + P338		
Warming 	Skin irritation Category 2	H315: Causes skin irritation	P264 P280	P302 + P352 P321 P332 + P313 P362 + P364	-	-

B.3. Eye damage and irritation

B.3.1. Definition

Serious eye damage means the production of tissue damage in the eye, or serious physical decay of vision, following application of a test substance to the anterior surface of the eye, which is not fully reversible within 21 days of application.

Eye irritation means the production of changes in the eye following the application of test substance to the anterior surface of the eye, which are fully reversible within 21 days of application.

Before any in vivo testing for serious eye damage/eye irritation is carried out, all existing information on a substance shall be reviewed. Preliminary decisions can often be made from existing data as to whether a substance causes serious (i.e. irreversible) damage to the eyes. If a substance can be classified on the basis of these data, no testing is required.

Table.2.28. Generic concentration limits of ingredients of a mixture classified as skin corrosive category 1 and/or eye category 1 or 2 for effects on the eye that trigger classification of the mixture for effects on the eye (category 1 or 2).

Sum of ingredients classified as:	Concentration triggering classification of a mixture as:	
	Irreversible Eye Effects	**Reversible Eye Effects**

	Category 1	Category 2
Eye Effects Category 1 or Skin Corrosive Category 1A, 1B, 1C	≥ 3 %	≥ 1 % but < 3 %
Eye Effects Category 2		≥ 10 %
(10 × Eye Effects Category 1) + Eye effects Category 2		≥ 10 %
Skin Corrosive Category 1A, 1B, 1C + Eye effects Category 1	≥ 3 %	≥ 1 % but < 3 %
10 × (Skin Corrosive Category 1A, 1B, 1C + Eye Effects Category 1) + Eye Effects Category 2		≥ 10 %

The mixture is classified for serious eye damage/eye irritation if the

Sum of (AConc / ACL) + (BConc / BCL) + …. + (ZConc / ZCL) is ≥ 1

Where AConc = the concentration of substance A in the mixture;

ACL = the concentration limit (either specific or generic) of substance A;

AConc = the concentration of substance B in the mixture;

BCL = the concentration limit (either specific or generic) of substance B; etc.

Table.2.29. Pictograms, signal words, hazard statements and precautionary statements for eye damage/irritation.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger 	Eye damage Category 1	H318: Causes serious eye damage	P280	P305 + P351 + P338 P310	-	-
Warming 	Eye irritation Category 2	H319: Causes serious eye irritation	P264 P280	P305 + P351 + P338 P337 + P313	-	-

B.4. Respiratory or skin sensitisation

B.4.1. Definition

Respiratory sensitizer means a substance that will lead to hypersensitivity of the airways following inhalation of the substance. Skin sensitizer means a substance that will lead to an allergic response following skin contact.

The hazard class Respiratory or Skin Sensitisation is differentiated into:

— Respiratory Sensitisation

— Skin Sensitisation.

The mixture shall be classified as a respiratory or skin sensitizer when at least one ingredient has been classified as a respiratory or skin sensitizer and is present at or above the appropriate generic concentration limit as shown in Table below for solid/liquid and gas respectively.

Table.2.30. Generic concentration limits of components of a mixture classified as either respiratory sensitizers or skin sensitizers that trigger classification of the mixture.

Component classified as:	**Generic concentration limits triggering classification of a mixture as:**		
	Respiratory sensitizer **Category 1**		**Skin sensitizer** **Category 1**
	Solid/liquid	**Gas**	**All physical states**
Respiratory sensitizer Category 1	≥ 1,0 %	≥ 0,2 %	
Respiratory sensitizer Sub-category 1A	≥ 0,1 %	≥ 0,1 %	
Respiratory sensitizer Sub-category 1B	≥ 1,0 %	≥ 0,2 %	
Skin sensitizer Category 1			≥ 1,0 %
Skin sensitizer Sub-category 1A			≥ 0,1 %

Skin sensitizer Sub-category 1B			≥ 1,0 %

Table.2.31. Pictograms, signal words, hazard statements and precautionary statements for respiratory or skin sensitizer.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger 	Respiratory sensitizer Category 1 and Subcategory 1 (A) and 1 (B)	H334: May cause allergy of asthma symptoms or breathing if inhaled	P261 P284	P304 + P340 P342 + P311	-	P501
Warming 	Skin sensitizer Category 1 and Subcategory 1 (A) and 1 (B)	H317: May cause an allergic skin reaction	P261 P272 P280	P302 + P352 P333 + P313 P321 P362 + P364	-	P501

B.5. Germ cell mutagenicity

B.5.1. Definition

A mutation means a permanent change in the amount or structure of the genetic material in a cell. The term ‘mutation’ applies both to heritable genetic changes that may be manifested at the phenotypic level and to the underlying DNA modifications when known (including specific base pair changes and chromosomal translocations). The term ‘mutagenic’ and ‘mutagen’ will be used for agents giving rise to an increased occurrence of mutations in populations of cells and/or organisms.

The more general terms ‘genotoxic’ and ‘genotoxicity’ apply to agents or processes which alter the structure, information content, or segregation of DNA, including those which cause DNA damage by interfering with normal replication processes, or which in a non-physiological manner (temporarily) alter its replication. Genotoxicity test results are usually taken as indicators for mutagenic effects.

The mixture shall be classified as a mutagen when at least one ingredient has been classified as a Category 1A, Category 1B or Category 2 mutagen and is present at or above the appropriate generic concentration limit as shown in Table below for Category 1A, Category 1B and Category 2 respectively.

Table.2.32. Generic concentration limits of ingredients of a mixture classified as germ cell mutagens that trigger classification of the mixture.

Ingredient classified as:	**Concentration limits triggering classification of a mixture as:**		
	Category 1 mutagen		**Category 2 mutagen**
	Category 1A	**Category 1B**	
Category 1A mutagen	≥ 0,1 %	—	—
Category 1B mutagen	—	≥ 0,1 %	—
Category 2 mutagen	—	—	≥ 1,0 %

The concentration limits in the table above apply to solids and liquids (w/w units) as well as gases (v/v units).

Table.2.33. Pictograms, signal words, hazard statements and precautionary statements for mutagen.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	Germ cell mutagenicity Category 1A	H340:May cause genetic defects	P201 P202 P280	P308 + P313	P405	P501
	Germ cell mutagenicity Category 1B					

Warming 	Germ cell mutagenicity Category 2	H341: Suspected of causing genetic defects	P201 P202 P280	P308 + P313	P405	P501

B.6. Carcinogenicity

B.6.1. Definition

Carcinogen means a substance or a mixture of substances which induce cancer or increase its incidence. Substances which have induced benign and malignant tumours in well performed experimental studies on animals are considered also to be presumed or suspected human carcinogens unless there is strong evidence that the mechanism of tumour formation is not relevant for humans.

The mixture will be classified as a carcinogen when at least one ingredient has been classified as a Category 1A, Category 1B or Category 2 carcinogen and is present at or above the appropriate generic concentration limit as shown in Table below for Category 1A, Category 1B and Category 2 respectively.

Table.2.34. Generic concentration limits of ingredients of a mixture classified as carcinogen that trigger classification of the mixture.

Ingredient classified as:	Generic concentration limits triggering classification of a mixture as:		
	Category 1 carcinogen		Category 2 carcinogen
	Category 1A	Category 1B	
Category 1A carcinogen	≥ 0,1 %	—	—
Category 1B carcinogen	—	≥ 0,1 %	—
Category 2 carcinogen	—	—	≥ 1,0 %

Note: If a Category 2 carcinogen is present in the mixture as an ingredient at a concentration ≥ 0,1 % a SDS shall be available for the mixture upon request.

Table.2.35. Pictograms, signal words, hazard statements and precautionary statements for carcinogenicity.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary StatementStorage**	**Precautionary Statement Disposal**
Danger 	Carcinogenicity Category 1A Carcinogenicity Category 1A	H350: May cause cancer	P201 P202 P280	P308 + P313	P405	P501
Warming 	Carcinogenicity Category 2	H351: Suspected of causing cancer	P201 P202 P280	P308 + P313	P405	P501

B.7. Reproductive toxicity

B.7.1. Definition

Reproductive toxicity includes adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring. The definitions presented below are adapted from those agreed as working definitions in IPCS/EHC Document No 225, Principles for Evaluating Health Risks to Reproduction Associated with Exposure to Chemicals. For classification purposes, the known induction of genetically based heritable effects in the offspring is addressed in Germ Cell Mutagenicity, since in the present classification system it is considered more appropriate to address such effects under the separate hazard class of germ cell mutagenicity.

In this classification system, reproductive toxicity is subdivided under two main headings:

(a) adverse effects on sexual function and fertility;

(b) adverse effects on development of the offspring.

The mixture shall be classified for effects on or via lactation when at least one ingredient has been classified as a Category 1A, Category 1B, Category 2 or additional category for effects on or via lactation and generic concentration limit as shown in Table below.

Table. 2.36. generic concentration limits of ingredients of a mixture classified as reproduction toxicants or for effects on or via lactation that trigger classification of the mixture.

Ingredient classified as:	**Generic concentration limits triggering classification of a mixture as:**			
	Category 1 reproductive toxicant		**Category 2 reproductive toxicant**	**Additional category for effects on or via lactation**
	Category 1A	**Category 1B**		
Category 1A reproductive toxicant	≥ 0,3 % [Note]			
Category 1B reproductive toxicant		≥ 0,3 % [Note]		
Category 2 reproductive toxicant			≥ 3,0 % [Note]	
Additional category for effects on or via lactation				≥ 0,3 % [Note]

<u>Note:</u> If a Category 1 or Category 2 reproductive toxicant or a substance classified for effects on or via lactation is present in the mixture as an ingredient at a concentration at or above 0,1 %, a SDS shall be available for the mixture upon request.

Table.2.37. Pictograms, signal words, hazard statements and precautionary statements for reproductive toxicity.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger	Reproductive toxicity Category 1A	H360: May damage fertility or	P201 P202	P308 + P313	P405	P501

	Reproductive toxicity Category 1B	the unborn child	P280			
Warming 	Reproductive toxicity Category 2	H361: Suspected of damaging fertility or the unborn child	P201 P202 P280	P308 + P313	P405	P501
-	Lactation effects	H362:May cause harm to breastfed children	P201 P260 P263 P264 P270	P308 + P313		

B.8. Specific target organ toxicity (STOT)

B.8.1. Definition

Specific target organ toxicity may occur for humans, i.e., by any route based on oral, dermal or inhalation

Specific target organ toxicity following a repeated exposure is classified as described in Specific target organ toxicity — Other specific toxic effects, listed below, are assessed separately and consequently are not included here:

(a) Acute toxicity

(b) Skin corrosion/irritation

(c) Serious eye damage/eye irritation

(d) Respiratory or skin sensitisation

(e) Germ cell mutagenicity

(f) Carcinogenicity

(g) Reproductive toxicity

(h) Aspiration toxicity.

The hazard class Specific Target Organ Toxicity — Single Exposure is differentiated into:

— Specific target organ toxicity — single exposure, Category 1 and 2;

— Specific target organ toxicity — single exposure, Category 3

Table.2.38. Guidance value ranges for single-dose exposures.

Route of exposure	**Units**	**Guidance value ranges for**		
		Category 1	**Category 2**	**Category 3**
Oral (rat)	mg/kg body weight	$C \leq 300$	$2\,000 \geq C > 300$	Guidance values do not apply [b]
Dermal (rat or rabbit)	mg/kg body weight	$C \leq 1\,000$	$2\,000 \geq C > 1\,000$	
Inhalation (rat) gas	ppmV/4h	$C \leq 2\,500$	$20\,000 \geq C > 2\,500$	
Inhalation (rat) vapour	mg/l/4h	$C \leq 10$	$20 \geq C > 10$	
Inhalation (rat) dust/mist/fume	mg/l/4h	$C \leq 1{,}0$	$5{,}0 \geq C > 1{,}0$	

Note: Guidance values are not provided for Category 3 substances since this classification is primarily based on human data. Animal data, if available, shall be included in the weight of evidence evaluation.

Table.2.39. for specific target organ toxicity-single exposure.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	STOT SE Category 1	H370: Causes damage to organs	P260 P264 P270	P308 + P311 P321	P405	P501

Warming 	STOT SE Category 2	H371: May causes damage to organs	P260 P264 P270	P308 + P311	P405	P501
Warming 	STOT SE Category 3	H335: May cause respiratory irritation H336:May cause drowsiness or dizziness	P261 P271	P304 + P340 P312	P403 + P233 P405	P501

The mixture shall be classified as a specific target organ toxicant (specific organ specified), following single exposure, when at least one ingredient has been classified as a Category 1 or Category 2 specific target organ toxicant and is present at or above the appropriate generic concentration limit as mentioned in Table below for Category 1 and 2 respectively.

Care shall be exercised when extrapolating toxicity of a mixture that contains Category 3 ingredient(s). A generic concentration limit of 20% is appropriate.

When a mixture contains a number of substances classified with Category 3 and present at a concentration below the Generic Concentration Limit (GLC), i.e. 20%, the concentrations of the individual substances with the same hazard (i.e. Respiratory Tract Irritation) are totalled separately. If each individual total is greater than the GCL then the mixture should be classified as Category 3 for that hazard.

Table.2.40. Generic concentration limits of ingredients of a mixture classified as a specific target organ toxicant that trigger classification of the mixture.

Ingredient classified as	**Generic concentration limits triggering classification of the mixture as**	
	Category 1	**Category 2**
Category 1 Specific Target Organ Toxicant	Concentration ≥ 10 %	1,0 % ≤ concentration < 10 %
Category 2 Specific Target Organ Toxicant		Concentration ≥ 10 %

Table.2.41. For specific target organ toxicity-repeated exposure.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Danger 	STOT RE Category 1	H372: Causes damage to organs	P260 P264 P270	P314	-	P501
Warming 	STOT RE Category 2	H373: May causes damage to organs	P260	P314	-	P501

B.9. Aspiration toxicity

B.9.1. Definition

'Aspiration' means the entry of a liquid or solid substance or mixture directly through the oral or nasal cavity, or indirectly from vomiting, into the trachea and lower respiratory system.

Aspiration toxicity includes severe acute effects such as chemical pneumonia, varying degrees of pulmonary injury or death following aspiration

Aspiration of a substance or mixture can occur as it is vomited following ingestion. This has consequences for labelling, particularly where, due to acute toxicity, a recommendation may be considered to induce vomiting after ingestion. However, if the substance/mixture also presents an aspiration toxicity hazard, the recommendation to induce vomiting shall be modified

Kinematic viscosity effects to the classification criteria. The conversion of dynamic viscosity to kinematic;

$$\frac{\text{Dynamic viscosity } (\text{mPa s})}{\text{Density } (\text{g/cm}^3)} = \text{Kinematic viscosity } (\text{mm}^2/\text{s})$$

A mixture which contains a total of 10 % or more of a substance or substances classified in Category 1, and has a kinematic viscosity of 20,5 mm2 /s or less, measured at 40^{o}C, shall be classified in Category 1.

In the case of a mixture which separates into two or more distinct layers, one of which contains 10 % or more of a substance or substances classified in Category 1 and has a kinematic viscosity of 20,5 mm /s or less, measured at 40^{o}C, then the entire mixture is classified in Category 1.

Table.2.42. Pictograms, signal words, hazard statements and precautionary statements for aspiration toxicity.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger 	Aspiration Category 1	H304: May be fatal if swallowed and enters airways.	-	P301 + P310 P331	P405	P501

C. Environmental hazards

C.1. Definition

Hazardous to the aquatic environment is differentiated into:

— acute aquatic hazard,

— long-term aquatic hazard.

The basic elements used for classification for aquatic environmental hazards are:

— acute aquatic toxicity,

— chronic aquatic toxicity,

— potential for or actual bioaccumulation, and

— degradation (biotic or abiotic) for organic chemicals.

Table.2.43. Classification categories for hazardous to the aquatic environment.

(a) Acute (short-term) aquatic hazard	
Category Acute 1:	
96 hr LC_{50} (for fish)	≤ 1 mg/l and/or
48 hr EC_{50} (for crustacea)	≤ 1 mg/l and/or
72 or 96 hr ErC_{50} (for algae or other aquatic plants)	≤ 1 mg/l. (Note 2)
(b) Long-term aquatic hazard	
(i) Non-rapidly degradable substances for which there are adequate chronic toxicity data available	
Category Chronic 1:	
Chronic NOEC or EC_x (for fish)	≤ 0,1 mg/l and/or
Chronic NOEC or EC_x (for crustacea)	≤ 0,1 mg/l and/or
Chronic NOEC or EC_x (for algae or other aquatic plants)	≤0,1 mg/l.
Category Chronic 2:	
Chronic NOEC or EC_x (for fish)	> 0,1 to ≤ 1 mg/l and/or
Chronic NOEC or EC_x (for crustacea)	> 0,1 to ≤ 1 mg/l and/or
Chronic NOEC or EC_x (for algae or other aquatic plants)	> 0,1 to ≤ 1 mg/l.
(ii) Rapidly degradable substances (Note 3) for which there are adequate chronic toxicity data available	
Category Chronic 1:	
Chronic NOEC or EC_x (for fish)	≤ 0,01 mg/l and/or
Chronic NOEC or EC_x (for crustacea)	≤ 0,01 mg/l and/or
Chronic NOEC or EC_x (for algae or other aquatic plants)	≤ 0,01 mg/l.
Category Chronic 2:	
Chronic NOEC or EC_x (for fish)	> 0,01 to ≤ 0,1 mg/l and/or
Chronic NOEC or EC_x (for crustacea)	> 0,01 to ≤ 0,1 mg/l and/or
Chronic NOEC or EC_x (for algae or other aquatic plants)	> 0,01 to ≤ 0,1 mg/l.
Category Chronic 3:	

Chronic NOEC or EC_x (for fish)	> 0,1 to ≤ 1 mg/l and/or
Chronic NOEC or EC_x (for crustacea)	> 0,1 to ≤ 1 mg/l and/or
Chronic NOEC or EC_x (for algae or other aquatic plants)	> 0,1 to ≤ 1 mg/l.
(iii) Substances for which adequate chronic toxicity data are not available	
Category Chronic 1: (Note 1)	
96 hr LC_{50} (for fish)	≤ 1 mg/l and/or
48 hr EC_{50} (for crustacea)	≤ 1 mg/l and/or
72 or 96 hr ErC_{50} (for algae or other aquatic plants)	≤ 1 mg/l. (Note 2)
and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log $K_{ow} \geq 4$).	
Category Chronic 2:	
96 hr LC_{50} (for fish)	> 1 to ≤10 mg/l and/or
48 hr EC_{50} (for crustacea)	> 1 to ≤10 mg/l and/or
72 or 96 hr ErC_{50} (for algae or other aquatic plants)	> 1 to ≤10 mg/l (Note 2)
and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log $K_{ow} \geq 4$).	
Category Chronic 3:	
96 hr LC_{50} (for fish)	> 10 to ≤ 100 mg/l and/or
48 hr EC_{50} (for crustacea)	> 10 to ≤ 100 mg/l and/or
72 or 96 hr ErC_{50} (for algae or other aquatic plants)	> 10 to ≤ 100 mg/l. (Note 2)
and the substance is not rapidly degradable and/or the experimentally determined BCF ≥ 500 (or, if absent, the log $K_{ow} \geq 4$).	

Mixtures can be made of a combination of both components that are classified (as Acute 1 and/or Chronic 1, 2, 3, 4) and others for which adequate toxicity test data is available. When adequate toxicity data are available for more than one component in the mixture, the combined toxicity of those components is calculated using the following additivity formulas (a) or (b), depending on the nature of the toxicity data:

a) Based on acute aquatic toxicity:

$$\frac{\sum \mathrm{Ci}}{\mathrm{L\,(E)\,C_{50m}}} = \sum_{n} \frac{\mathrm{Ci}}{\mathrm{L\,(E)\,C_{50i}}}$$

Where:

C_i=concentration of component i (weight percentage);

$L(E)C_{50i}$ = (mg/l) LC50 or EC50 for component i;

η = number of components, and i is running from 1 to n;

$L(E)C_{50m} = L(E)\ C_{50}$ of the part of the mixture with test data.

The calculated toxicity may be used to assign that portion of the mixture an acute hazard category which is then subsequently used in applying the summation method;

(b) Based on chronic aquatic toxicity:

$$\frac{\sum Ci + \sum Cj}{EqNOECm} = \sum_{n} \frac{Ci}{NOECi} + \sum_{n} \frac{Cj}{0{,}1 \times NOECj}$$

Where:

C_i = concentration of component i (weight percentage) covering the rapidly degradable components;

Cj = concentration of component j (weight percentage) covering the non- rapidly degradable components;

NOECi = NOEC (or other recognised measures for chronic toxicity) for component i covering the rapidly degradable components, in mg/l;

NOECj = NOEC (or other recognised measures for chronic toxicity) for component j covering the non-rapidly degradable components, in mg/l;

n = number of components, and i and j are running from 1 to n;

EqNOECm = Equivalent NOEC of the part of the mixture with test data.

Table.2.44. Classification of a mixture for long-term hazards, based on summation of the concentrations of classified components.

Sum of components classified as	**Mixture is classified as**
Chronic 1 × M () ≥ 25 %	Chronic 1
(M × 10 × Chronic 1) + Chronic 2 ≥ 25 %	Chronic 2
(M × 100 × Chronic 1) + (10 × Chronic 2) + Chronic 3 ≥ 25 %	Chronic 3
Chronic 1 + Chronic 2 + Chronic 3 + Chronic 4 ≥ 25 %	Chronic 4

Table.2.45. Pictograms, signal words, hazard statements and precautionary statements.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement Prevention**	**Precautionary Statement Response**	**Precautionary Statement Storage**	**Precautionary Statement Disposal**
Warming 	Aquatic Acute 1	H400: Very toxic to aquatic life	P273	P391	-	P501
Warming 	Aquatic Chronic 1	H410: Very toxic to aquatic life with long-lasting effects	P273	P391		P501
-	Aquatic Chronic 2	H411: Toxic to aquatic life with long-lasting effects	P273	P391	-	P501
-	Aquatic Chronic 3	H412: Harmful to aquatic life with long-lasting effects	P273	-	-	P501
-	Aquatic Chronic 4	H413:May cause long lasting harmful to aquatic effects	P273	-	-	P501

D. Additional hazards

D.1. Hazardous to the ozone layer

D.1.1. Definition

Ozone depleting potential (ODP) is an integrative quantity, distinct for each halocarbon source species, that represents the extent of ozone depletion in the stratosphere expected from the halocarbon on a mass-for-mass basis relative to CFC-11. The formal definition of ODP is the ratio of integrated perturbations to total ozone, for a differential mass emission of a particular compound relative to an equal emission of CFC-11.

Table.2.46. Generic concentration limits for substances (in a mixture), classified as hazardous to the ozone layer (category 1), that trigger classification of the mixture as hazardous to the ozone layer (category 1).

Classification of the substance	**Classification of the mixture**
Hazardous to the ozone layer (Category 1)	$C \geq 0{,}1$ %

Table.2.47. Pictograms, signal words, hazard statements and precautionary statements.

CLP pictogram and signal word	**Hazard class and category**	**Hazard statement**	**Precautionary Statement** **Prevention**
Warming 	Ozone	H420: Harms public health and the environment by destroying ozone in the upper atmosphere	P502

2.2.1.5. Hazard labelling and packaging according to the CLP regulation

A. Definition [10]

All dangerous chemicals (substances and mixtures) on the market must be classified, labelled and packaged according to the CLP Regulation (EC) No. 1272/2008 by 1st June 2015.

The liable side for labelling and packaging of dangerous substances and mixtures are:

- manufacturers of chemicals,
- importers of chemicals or mixtures,
- formulators of mixtures, and
- distributers or end Users, who do not reformulate or change the chemicals or mixtures but relabel or repackage them.

B. Materials not included in CLP

Waste and cosmetics, medicines, medical devices, veterinary products, foodstuffs or animal feed in finished state, for the final user are not included in CLP Regulation

C. Classification of hazardous chemicals/mixtures

The physical properties and health with environmental effects of chemicals must be defined and evaluated if they need to be included in regulations. Some dangerous materials already have agreed classifications that are listed in Annex VI of the CLP Regulation.

If a chemical material seems not to have a classification listed in Annex VI, then the producer or importer has to investigate all available information about the CLP classification criteria and classify the dangerous material when a criterion is met.

Similarly, formulators or importers of mixtures must Investigate all relevant information about the CLP classification criteria and classify dangerous mixtures.

Once the chemicals dangers are identified, Hazard labels must be provided and the chemical must be contained in packaging that meets the requirements of CLP.

D. Labelling of dangerous substances/mixtures

A label must contain the following information applicable to the substance or mixture placed on the market as shown in figure 2.20.

- **name, address and telephone number** of the EU supplier(s),
- **product identifiers** e.g. chemical name and CAS/EC no. of the substance/trade name of a mixture along with the chemical name(s) of all substances responsible for classification of the mixture (excluding skin and eye irritants),
- **hazard pictogram(s1)**: signal word: either Warning or Danger depending on theClassification,

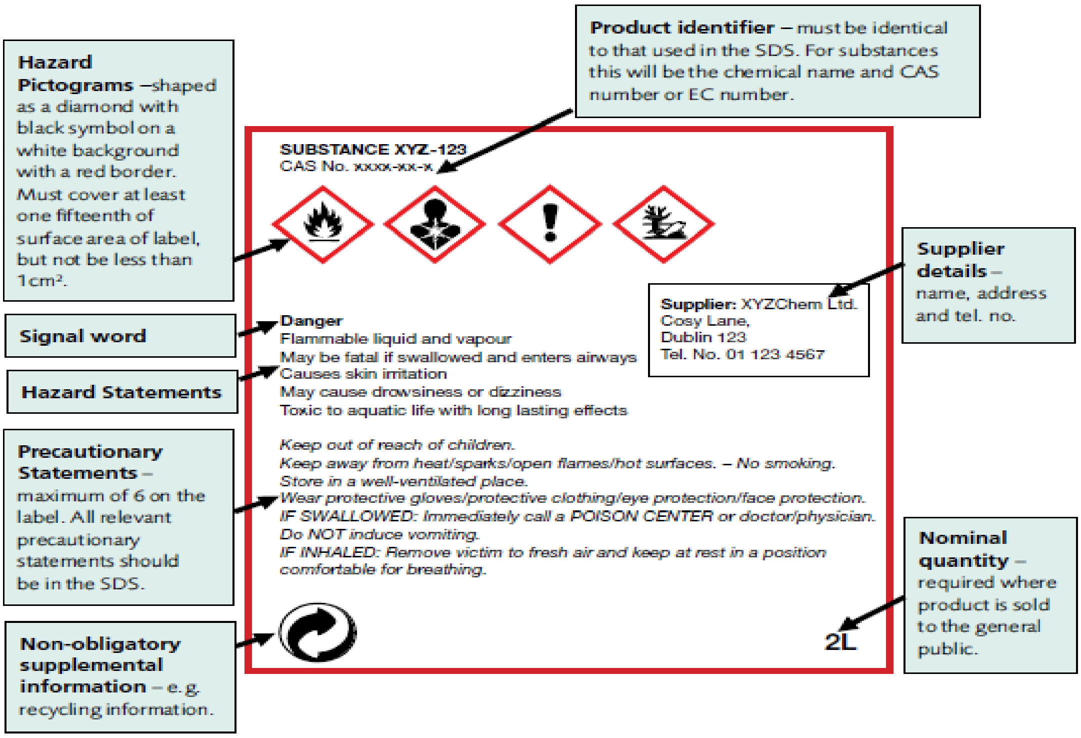
- **hazard statement(s)** description of the dangerous effect; for example; Harmful if inhaled,
- **precautionary statements** to İnform the user of the chemical to take precautions to protect health/environment e.g. Keep out of reach of children,
- **nominal quantity** (when the chemical is supplied to the general public), and
- **additional information**.

Obligatory additional information includes hazard statements taken from the previous chemical classification e.g.'' EUH001 Explosive when dry. May cause an allergic reaction".

Optional additional labelling information, for example, instructions for use is not a legal requirement under CLP. However, if provided it must not distract from nor contradict the obligatory label elements, danger and precautionary statements. Statements like 'nontoxic', 'non-polluting' cannot be used on labels.

The danger information on the label must be consistent with the classification in Section 2.1 and the label in Section 2.2 of the Safety Data Sheet (SDS) provided for the same product.

Figure. 2.21. Example of hazard label for supply.



Hazard Pictograms –shaped as a diamond with black symbol on a white background with a red border. Must cover at least one fifteenth of surface area of label, but not be less than 1cm².

Product identifier – must be identical to that used in the SDS. For substances this will be the chemical name and CAS number or EC number.

SUBSTANCE XYZ-123
CAS No. xxxx-xx-x

Supplier: XYZChem Ltd.
Cosy Lane,
Dublin 123
Tel. No. 01 123 4567

Supplier details – name, address and tel. no.

Signal word

Hazard Statements

Danger
Flammable liquid and vapour
May be fatal if swallowed and enters airways
Causes skin irritation
May cause drowsiness or dizziness
Toxic to aquatic life with long lasting effects

Keep out of reach of children.
Keep away from heat/sparks/open flames/hot surfaces. – No smoking.
Store in a well-ventilated place.
Wear protective gloves/protective clothing/eye protection/face protection.
IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
Do NOT induce vomiting.
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

Precautionary Statements – maximum of 6 on the label. All relevant precautionary statements should be in the SDS.

Non-obligatory supplemental information – e.g. recycling information.

2L

Nominal quantity – required where product is sold to the general public.

E. Layout and dimensions of the hazard label

- Be firmly attached to the surface of product
- Be visible, legible and readable and dimensions;
- Have the following dimensions;

Table.2.48. Layout and dimensions of the hazard label.

Capacity of the package	Dimensions of label (in millimetres)	Dimension of each pictogram (in millimetres)
≤ 3 litres	If possible at least 52x74	Not smaller than 10x10 If possible ,at least 16x16
>3 litres but ≤ 50 litres	At least 74x105	At least 23x23
>50 litres but ≤ 500 litres	At least 105x148	At least 32x32
>500 litres	At least 148x210	At least 46x46

- have all the danger pictograms, signal word, hazard and precautionary warnings together,
- if, where more than one language is used, Same language warnings shall be grouped together,
- be sure that hazard pictogram can be seen clearly (black print on white background,
- surrounded by red frame being at least one fifteenth and at least 1 cm2 of the label), and
- have no blank pictograms (where blank pictograms are unavoidably printed on the label they should be blacked out).

Figure. 2.22. Hazard label for drum.

F. Updating the hazard label

When there is a change in classification label should be updated without delay, especially if the result leads to a more severe danger or where new additional information is required on the label because of the change. Other required label changes e.g. change in supplier address shall be done within 18 months of the required change. Suppliers should cooperate to ensure that labels are updated without any delay.

G. Labelling of workplace chemicals

The requirement for a CLP danger label is dependent on if the chemical is being placed on the market or not, noting that import is deemed to be ‘placing on the market’

All incoming or outgoing materials to or from a workplace needs a CLP hazard label if they are being ‘placed on the market’. So, all incoming materials to a workplace should be labelled by the supplier, and all outgoing chemicals from a workplace should be labelled before being placed on the market.

However, if the materials for chemicals produced and used within a workplace’, because they are stored and transported in the workplace and not being placed on the market, the CLP hazard labelling rules do not apply [11].

However, there is still a requirement to ensure a risk-based approach to be undertaken to determine any potential hazards from such chemicals produced, stored, transported and used within the workplace. This results in a requirement to produce an ‘in-house’ hazard label.

Workplace chemicals come under the remit of the Chemical Agent and Work Place Signs Regulations. These Regulations will be amended before 1st June 2015 to align them with CLP.

H. Chemicals without packaging

a new provision under CLP for ‘wet cement’ which is sold to the general public without packaging’. It must be with a copy of the label elements required under CLP (see part 5 Annex II of the CLP Regulation for more information.

I. Revisions from labelling

Derogations from danger labelling requirements are permitted in special cases including transportable gas cylinders, gas containers intended for propane, butane or liquefied petroleum gas, certain aerosols, certain mixtures containing elastomers and explosives (See section of the CLP Regulation for further details).

J. Exemptions from labelling

Certain labelling elements may be omitted when contents do not exceed 125ml, depending on the danger classification of the chemical or mixture (see Section 1.5 Annex I of the CLP Regulation for more information).

Where packaging is either in such a shape or form or so small as to not allow the necessary hazard labelling information to fit on the label, derogation exists. In such cases and where applicable, the label elements may be provided either on:

- fold-out labels, or on
- tie-on tags, or on
- outer packaging.

Where the label for the outher packaging is fully compliant all label elements for certain hazard classes which do not exceed 25ml may be omitted from soluble packaging for single use except biocides and plant protection products.

Also an exemption applies for chemicals supplied for R&D or Quality Control analysis where the contents of the inner package do not exceed 10ml and where the label of the outer packaging is fully compliant.

K. Danger labels for supply and transport

K.1. Outer and inner packaging classified for supply (not for transport)

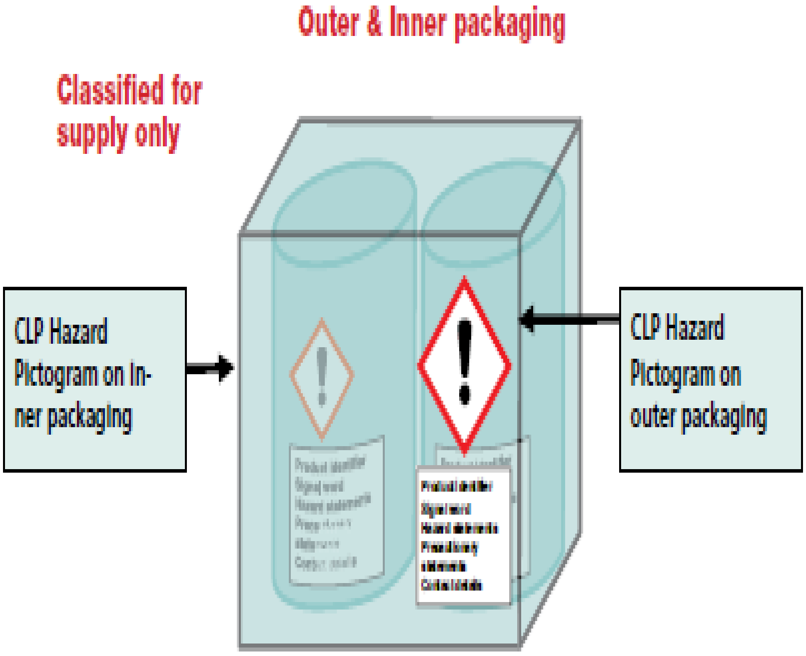
If chemicals and mixtures are not considered dangerous for transport they are not required to be classified and labelled according to the CLP Regulation require classification and labelling under the provisions of the transport of dangerous goods legislation.

Substance and mixtures which are not required to be classified and labelled under the provisions of the transport of dangerous goods need to still display CLP labels on the inner, intermediate and outer packaging.

This is a new rule of CLP Regulation as the old rules, the outer packaging would previously have been left blank if transport rules did not apply, which meant that it was not apparent that a dangerous substance or mixture was being transported.

An example of a product which does not require classification or labelling under the transport of dangerous goods rules would be a mixture which is classified for supply, as being harmful or causing skin sensitization. See figure 2.22 for the labelling required on outer and inner packaging for a substance or mixture classified under supply legislation but not under transport legislation.

Figure.2.23. Substance or mixture classified under supply legislation but not under transport legislation.

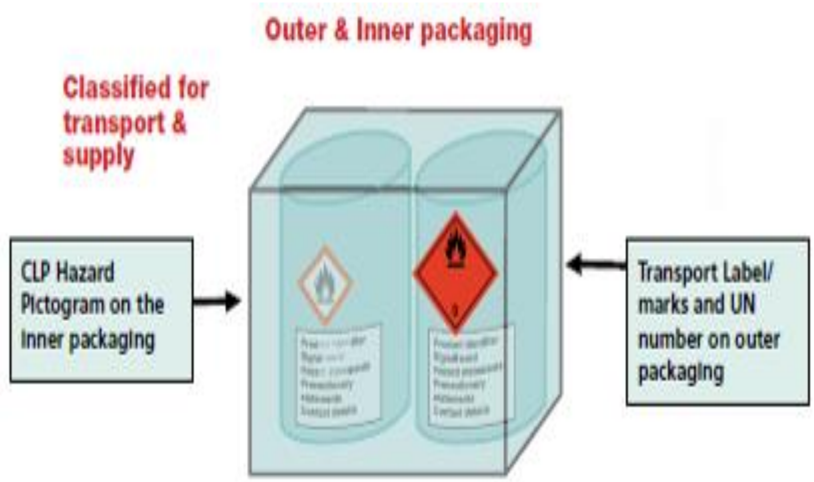


K.2. Outer and inner packaging classified for both transport and supply

If labelling is required under both the provisions of the transport of dangerous goods legislation and under the CLP Regulation for the same danger, and the package consists of an outer and inner packaging, the outer packaging must display the transport label elements but the CLP supply labelling on the outer packing is optional.

But the inner and intermediate packaging must be labelled in accordance with CLP. See figure 2.23 for an example of the labelling required on outer and inner packaging for a substance or mixture classified under both supply and transport legislation.

Figure.2.24. Substance or mixture classified under both transport and supply legislation.

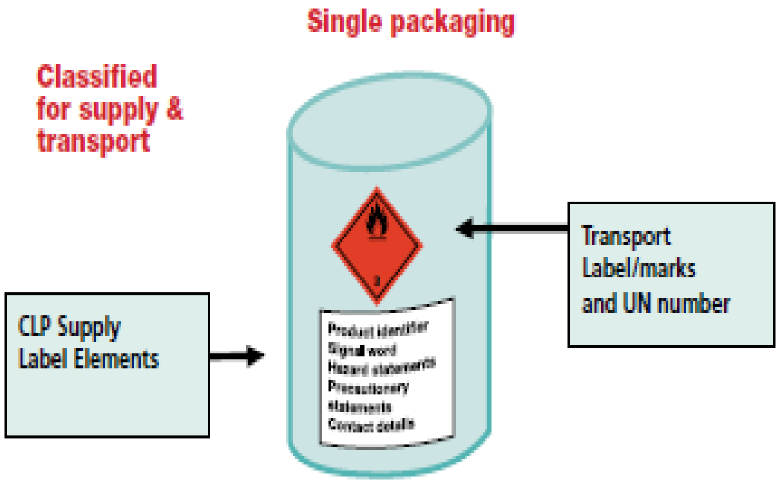


K.3. Single packaging classified under both supply and transport

If there is no inner packaging (single packages), labelling under the provisions of both the transport of dangerous goods legislation and the CLP Regulation is required.

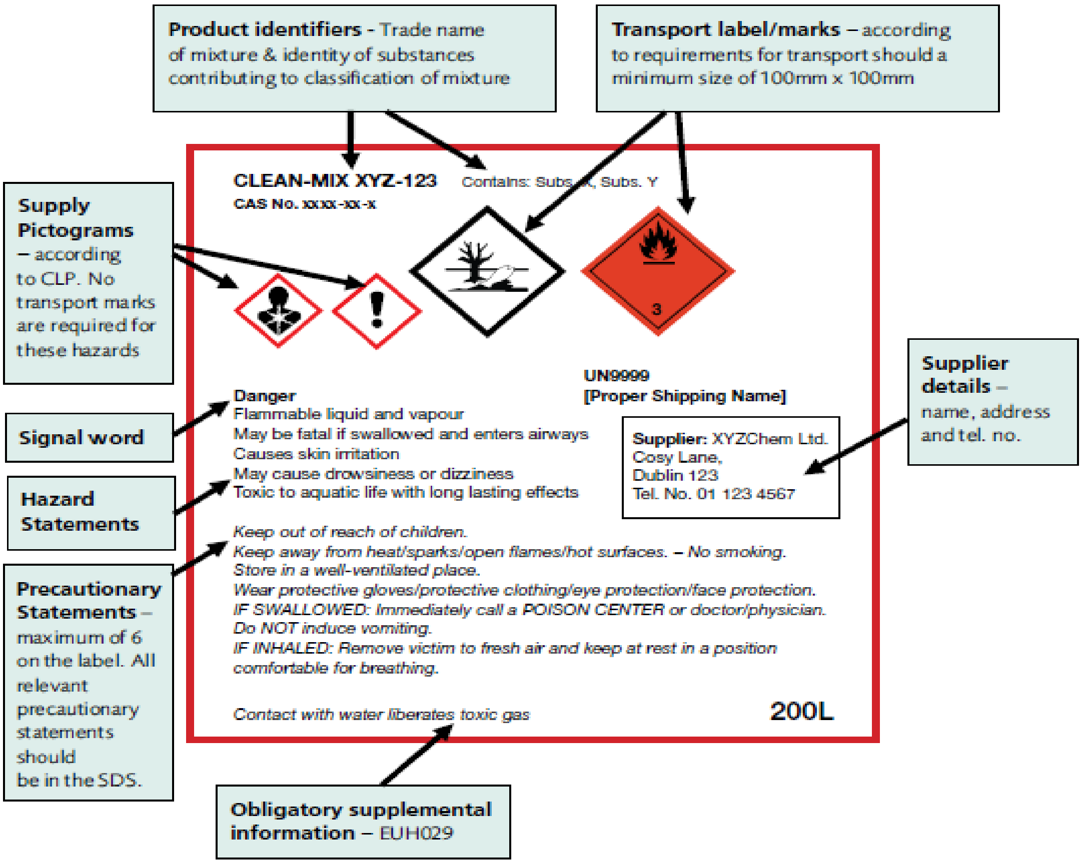
If the hazard pictograms for transport and CLP are the same, the CLP pictogram(s) need not appear. Figure 4 depicts a single package that is classified under both transport and supply legislation. While the CLP pictogram has been omitted, the CLP supply label elements shall still be provided below the transport pictogram, as demonstrated in Figure 2.24.

Figure.2.25. Single packaging classified under both supply and transport legislation.



An example of a single packaging label (for a 200 litre drum) for a mixture classified under both transport and CLP criteria. Transport and CLP labels must be shown on the packaging. The CLP pictograms for flammability, dermal toxicity and aquatic dangers (acute and chronic) have been omitted as the underlying hazards are already covered by the corresponding transport pictograms.

K.4. Transport labels/marks take precedence over a clp pictogram on single packaging.



Product identifiers - Trade name of mixture & identity of substances contributing to classification of mixture

Transport label/marks – according to requirements for transport should a minimum size of 100mm x 100mm

Supply Pictograms – according to CLP. No transport marks are required for these hazards

Signal word

Hazard Statements

Precautionary Statements – maximum of 6 on the label. All relevant precautionary statements should be in the SDS.

Supplier details – name, address and tel. no.

Obligatory supplemental information – EUH029

CLEAN-MIX XYZ-123 Contains: Subs. X, Subs. Y
CAS No. xxxx-xx-x

UN9999
[Proper Shipping Name]

Danger
Flammable liquid and vapour
May be fatal if swallowed and enters airways
Causes skin irritation
May cause drowsiness or dizziness
Toxic to aquatic life with long lasting effects

Supplier: XYZChem Ltd.
Cosy Lane,
Dublin 123
Tel. No. 01 123 4567

Keep out of reach of children.
Keep away from heat/sparks/open flames/hot surfaces. – No smoking.
Store in a well-ventilated place.
Wear protective gloves/protective clothing/eye protection/face protection.
IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
Do NOT induce vomiting.
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

Contact with water liberates toxic gas

200L

K.5. Packaging of dangerous substances/mixtures

Packaging should be designed so the hazardous contents cannot leak, except where more specific safety devices are required to be in place. the packaging material shall be strong enough to withstand normal stress and strains during handling.

Depending on the classification of the material or mixture Child-resistant fastenings and tactile warnings of danger may be required for certain dangerous chemicals. Details of which is set out in Annex II of CLP.

Replaceable fastenings should be designed so that they can be repeatedly refastened without the contents escaping.

When sold to the general public the packaging should not have a shape or a design that would attract or arouse the active curiosity of children or be misleading to consumers. It should not have a similar design to that is used in foodstuff, animal feed, medicines or cosmetics.

<u>Note:</u> Packaging that meets the requirements of the rules of the transport of dangerous goods shall meet most of the provisions of the CLP.

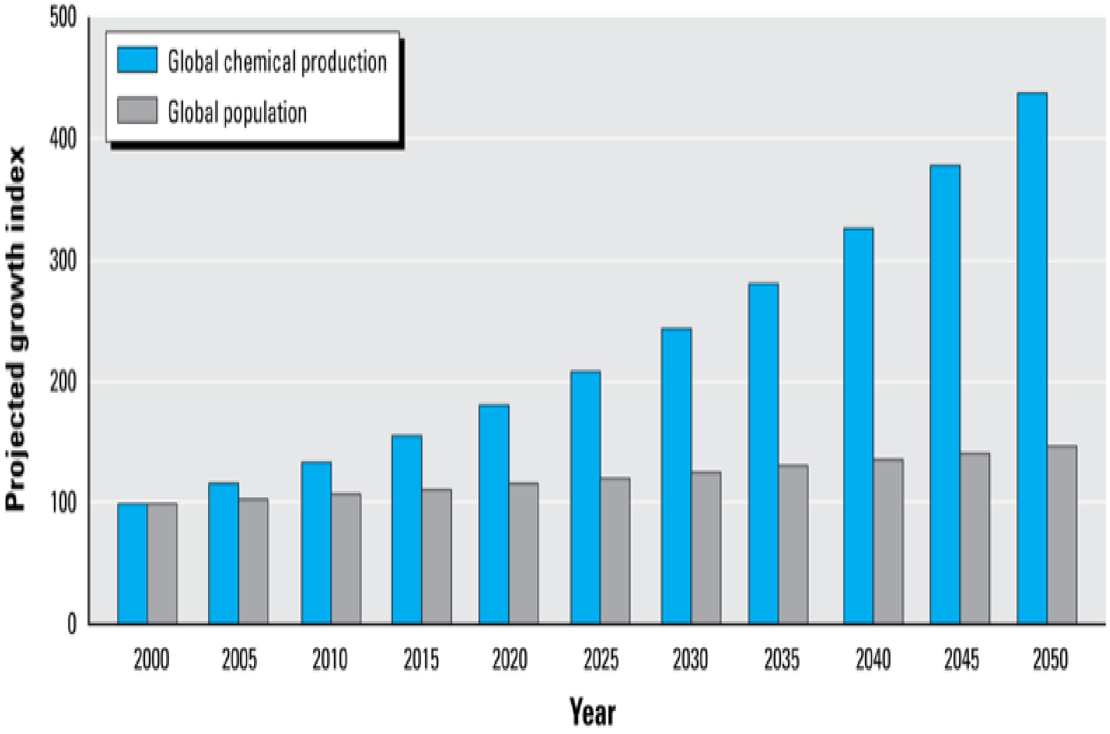
Figure.2.26. the Rules of the Transport of Dangerous Goods.

2.2.2. The REACH System

2.2.2.1. Introduction

Modern industrial manufacturing processes and modern societies need to use chemical substances. Chemistry and chemical products are described as the key elements in development of modern societies [1]. Thus, production of chemicals and their usage are getting increased through the worldwide. As an example, the global output of chemicals increased approximately 10 folds between 1970 and 2010 [2]. According to official estimates, the increase in chemical production will have been seriously raised by 2050. A grow rate of 3% per year is estimated and it is rapidly outpaced the rate of global population growth, which is guessed at 0.77% per year (Fig. 1) [3]. For example, the chemical industry is Europe's third largest manufacturing industry. It employs 1.7 million people directly and up to 3 million jobs are dependent on it.

Figure. 2.27. Global chemical production growth [3].



Many useful products are produced for modern society and the chemicals are often used in their production. Their production, storage, transport, usage and disposal may also involve in risks that lead to major accidents. Whole of a town, a city and/or a county can be threatened by an explosion in a chemical plant. Similarly, whole of a coast by the shipwreck of a tanker and whole of a region by the leaks from a chemical installation can be affected. The examples are follows: Bhopal (1984) was the scene of the accident with the most human casualties; the Basel warehouse fire (1986) caused large-scale pollution of the Rhine; and the Baia Mare spill (2000) severely threatened the Danube River. More recently, the populations and the towns of Enschede (2000) and Toulouse (2001) were seriously affected by chemical explosions, spill or disaster [4-5-6].

The Bhopal Disaster was a gas leak case in India on 1984 and it was considered as the world's worst industrial disaster at that time. About 500.000 people as a result of this disaster was exposed to methyl isocyanate (MIC) gas and other chemicals (Photo. 2.1).

Photograph.2.1. The Bhopal disaster.

The Sandoz blaze was occurred as a result of a chemical spill in Switzerland on 1986 and it is considered as a major environmental disaster (Photo. 2.2).

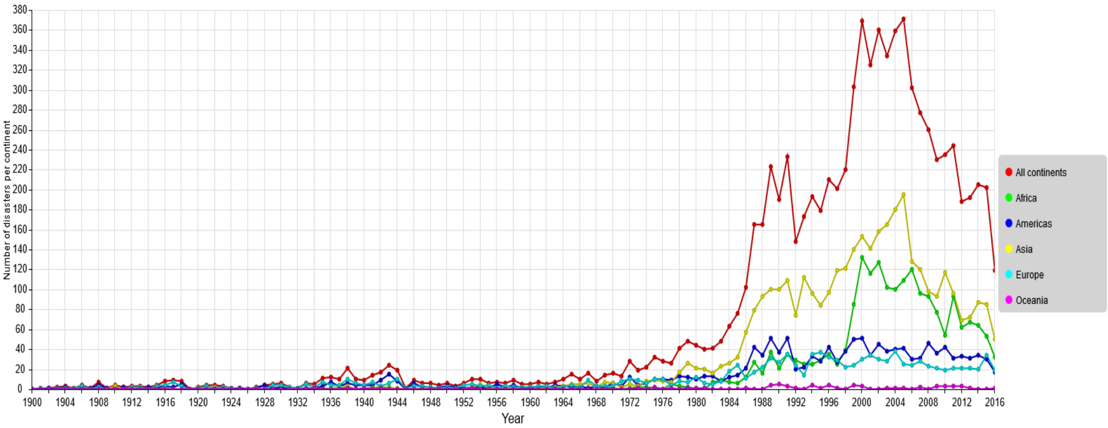
Photograph. 2.2. The Sandoz chemical spill.

The Baia Mare spill was a leak of cyanide in Romania on 2000 and this case has been called the worst environmental disaster in Europe since the Chernobyl disaster (Photo. 2.3).

Photograph. 2.3. The Baia Mare spill.

Although measures are being taken, it continues occurred to disasters resulting in chemical explosions or spill.

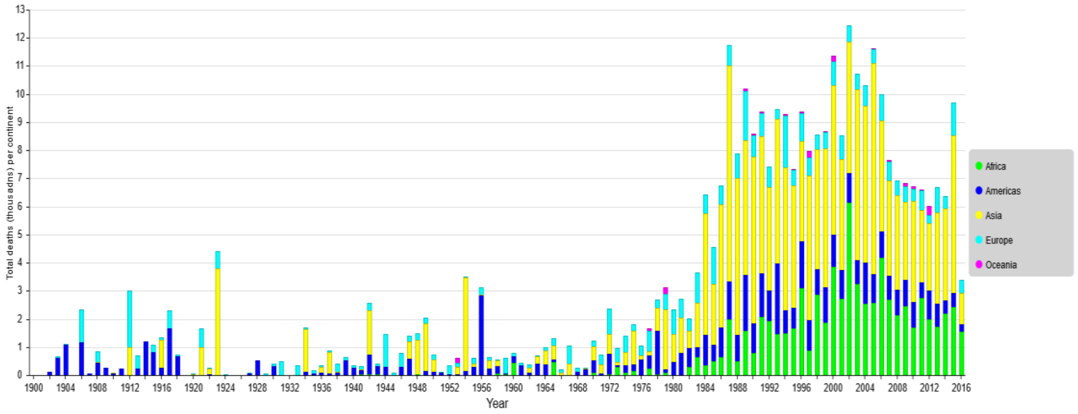
Figure.2.28. Total number of reported technological disasters between 1900 and 2016 [4].



EM-DAT: The OFDA/CRED International Disaster Database - www.emdat.be - Universite Catholique de Louvain, Brussels - Belgium

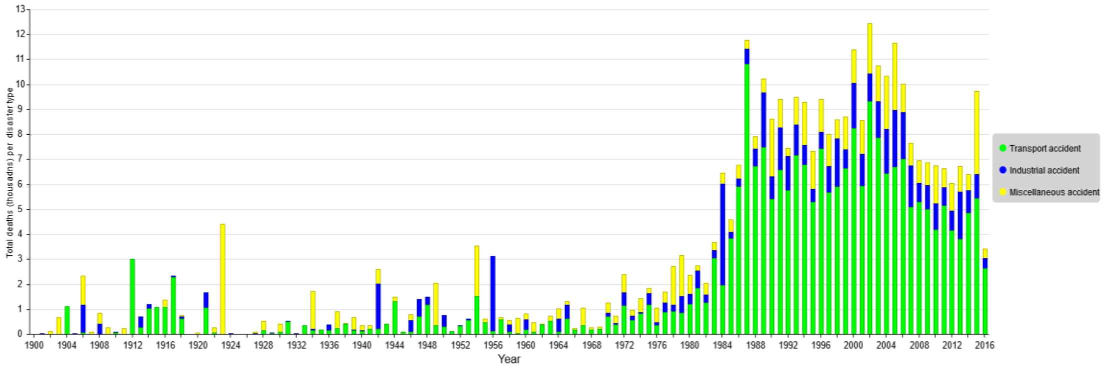
The technological disasters have been continued to major losses in terms of property damages and deaths. Hence, in addition to financial losses as a result of such events may be occured negative consequences for environment and living (Figure 27 and 28).

Figure. 2.29. Total deaths caused by reported technological disasters between 1900 and 2016 (according to the continent) [5].



EM-DAT: The OFDA/CRED International Disaster Database - www.emdat.be - Universite Catholique de Louvain, Brussels - Belgium

Figure. 2.30. Total deaths caused by reported technological disasters between 1900 and 2016 (according to the accident types) [6].



EM-DAT: The OFDA/CRED International Disaster Database - www.emdat.be - Universite Catholique de Louvain, Brussels - Belgium

2.2.2.2. Aim and implementation of the REACH

REACH is a new policy on management of chemicals in The European Union.

REACH is an abbreviation used in the form of Registration, Evaluation, Authorisation and Restriction of Chemicals.

REACH Regulation was accepted in co-voting on December 18, 2006 in The European Union (Number:EC 1907/2006).

It was published on May 29, 2007 in the Official Journal of the European Union after text edits (Number: L136).

As of June 1, 2007 has entered into force in countries of The European Economic Community (EEC) and The European Free Trade Association (EFTA).

The chronological order of these approaches adopted by European Union is given as follows (Figure 2.30) [7].

The REACH Regulation has brought for protection in terms of risks of chemical substances.

It has also provided to bring the highest level of protection to human health and the environment.

In addition, it will be provided in increase in innovation and competition in domestic market of the European Union [8].

Figure.2.31. The History of the adoption process for the new chemicals legislation (it was collected from alternatives sources) [7].

On 13th February, 2001.
- The European Commission adopted a White Paper setting out the strategy for a future Community Policy for Chemicals.

On 29 October, 2003 .
- The European Commission's original legislative proposal on REACH COM(03) 644 (01) and COM(03) 644 (02) amending Directive 67/548/EEC.

On 17 November, 2005.
- The work in the European Parliament has been led by the Committee on the Environment, Public Health & Food Safety, with – in first reading - the assistance of nine other parliamentary committees. The European Parliament adopted its first reading opinion.

On 13 December, 2005.
- The Council reached a Political Agreement for a Common Position.

On June 2006.
- The Environment Council formally adopted the Common Position.

On 12 July, 2006.
- A Commission Communication on the Common Position (COM (2006) 375).

On December, 2006.
- The representatives of the European Parliament and the Council found a negotiated agreement of the final version of REACH.
- This agreement was subsequently endorsed at second reading in the European Parliament on 13 December 2006 and got finally adopted at the Environment Council on 18 December 2006.

On 30 December, 2006.
- The text of the law was published in the Official Journal of the European Union L 396.

On 1 June, 2007.
- The new EU chemicals Regulation REACH entered into force.

On 1 June, 2008.
- The new European Chemicals Agency in Helsinki, Finland, will be fully operational on 1 June 2008, in time for the industry's obligation to submit pre-registration dossiers for existing substances and registration dossiers for new substances.

2.2.2.3. Overall approach of the REACH

- Protecting environment and human health,
- To determine to responsibles in terms of manufacturer and importer / exporter,
- Free movement of substances in the European Union markets,
- To increase in competition and innovation in chemical industry of the European Union.

2.2.2.4. The main principles of the REACH

- Registration: Registrating to The REACH of chemical substances,
- Evaluation: The evaluation of registrating documents and substances.
- Authorisation: Authorization of substances.
- Restriction: Restriction and prohibition of chemical substances [9].

2.2.2.5. The operation of the REACH

It was taken from official authorities to evidence obligation of chemical substances and it was given to industry. Previously responsibilities were in public institutions. Now, the producers and the importers within the EU has been obliged with evidence to harmless for environment of chemical substances.

There are rules “no data, no market” in REACH [10]. This means that it should be registered in a central database of chemicals within the EU (for manufacturing and importing). If it is not registrating process, it will be prohibited to producing, importing and using in the EU of chemicals.

The data related to chemicals should be produced according to standards of Good Laboratory Practices (GLP). At the same time, it can be accepted at matching standards with OECD and High Production Volume.

The European Chemicals Agency (ECHA) was established in Helsinki on June 1, 2007. The European Chemicals Agency is responsible for managing and monitoring of its implementation of the REACH System [11].

Trading and using of SVHC is granted with special permission along with the licensing process. The lists are published on website of The ECHA [12].

There is rule “Single registration for the same substance”. Thus, it will be prevented repeating registration. In addition, between applicants is provided sharing of data related to substances.

If there are significantly risks in terms of human health and environment, it can be taken limitations by authorities of member states. Moreover, measures can be taken.

Datas in registration files will be examined and evaluated by ECHA and member countries.

2.2.2.6. The general conditions for the REACH

Implemented of REACH can be summarized as follows:

- It will be applied to producers or importers, if there are chemical substances in structure of a product (or preparat).
- It will be applied to intermediate user of substances.
- It will be applied to chemical substances between 30.000 and 100.000 in number in the markets.
- It will be applied to chemical substances with high risk of number of about 1500.

2.2.2.7. The special conditions for the REACH

REACH has an approach based on substances. Responsibilities are directly implemented on substances (instead of on their own or in a mixture).

There are some exceptions in REACH, but it is implemented to all substances. Substances out of scope can be summarized as follows:

- Radioactive substances,
- Substances under custom control,
- Transport of substances,
- Nonisolated intermediate products.

There are special rules for substances used in research and development and in registration of isolated intermediates.

Table.2.49. Typically, the Identity of a substance (It was given as an example).

A chemical name	Benzene
A number	EC number 200-753-7
A chemical composition*	>99 % benzene and <1% toluene
*The composition is determined by chemical analysis.	

2.2.2.8. Substances on their own or in a mixture

REACH deal with concept substances. Most of obligations are adopted based on substances whether own or a mixture. A substance is defined as a chemical element. Its components occurred naturally or as a result of any process. They are included in this definition any additive introduced to protect stability of substance.

However, it is not considered to be any solvent component that can be separated without affecting the stability of substance or altering its composition.

If more than two substances are mixed in such a way as to form a mixture or a solution, it is used the term 'preparat'.

They are obligations for registration to the Agency of producers or importers for each substance produced over 1 tonne per year (and/or if it is bringing from outside the EU).

At the same time, it is applied to substances produced or imported. It is requested of preparation of exposure scenarios for formulators under certain conditions.

2.2.2.9. Substances in articles

There is a special regime for substances in articles for registration under REACH. An article under REACH is a legal term expressing any object that given a specific shape or design to be used for a specific purpose (like car, textile, electronics, etc.).

In REACH, if there are production or import in quantities exceeding 1 ton / year, all substances will be recorded according to normal rules. In addition, all substances for candidate list should be reported to the Agency, if ratio in the article is more than 0.1% and over 1 tonne per year.

If it can be prevented to exposure to people and environment, there isn't required to reporting in normal conditions. It must be provided at information for safe use in these situations. Informations on notification of a substance are given as follows.

- Identity of the person of reporting,
- Identity of substance,
- Classification of substance,
- Labelling of substance,
- Aim of use (in brief),
- Tonnage.

If there is a risk for human health and environment, it can request of registration for substance in article by the Agency. In addition, it should be provided sufficient information by the supplier to ensure to safe use of substances (for the article containing a SVHC (more than 0.1%)

2.2.2.10. Intermediate products

They are intended to be consumed or converted into another chemical substance of intermediate products and it isn't planned to take place inside last product.

There is a simple (light) register for isolated specific intermediates. REACH requires that only certain risk information be sent to the Agency. It should be registered intermediate products isolated in place. However, if there is strict control, it requires less information. Registered informations should be as follows.

- Hazard class,
- Any information available on the substance,
- Risk assessment measures and information about recommendations.

Datas on existing risk management measures is implemented or recommended, but it isn't required for a chemical safety assessment. They have been exempted from authorization procedure, but it may be subject to substance evaluation by Member States.

It should be recorded isolated intermediates (intermediates carried under controlled conditions between areas). If it is under strict control or used, it requires less information.

If intermediate products under controlled conditions is carried in quantities of 1000 tonnes or more, it will be higher potential exposure risk. It should be added datas in annex VII of REACH Regulation to recording file in this instance.

2.2.2.11. Polymers

Polymers occurs with the recurrence (monomers) of weight units in low molar (like plastic) as structure.

Polymers can potentially cause to recorded in a large numbers and it is considered that will be at low risk due to their structure. Therefore, significant substances for provide to workability are exempt from registering and evaluating. However, polymers may be subject to authorization and restriction.

At the same time, if it is provided both of the following conditions, polymers producers and importers must be registered to the agency for unregistered monomers or other unregistered substances.

- If Polymer contains more than 2% by weight (w/w) of monomer or other substance,
- If amount of this monomer or other substance is totally 1 tonne or more per year.

2.2.2.12. Research and development

Under REACH there isn't obligated to registered of substances below one tonne per year.

One of aims of REACH given to supported to researchs and developments for increased of innovation capacity of industries. Therefore, there are exemptions under REACH.

Scientific research and development under REACH is any scientific experiment for investigation or chemical research that carried out under controlled conditions below 1 tonne per year. Simply, there are exemptions for substances used in this research and development.

If it is notified to the agency, substances using and producing for research and development (PPORD) will be exempt from registering. It will be paid a fee to the agency for this notified.

This exemption may be valid for up to 5 years. The agency can extend up to 5 years of exemption period based on application. However, it can be requier that this research and development program can be proved by applicant. The Agency will check to completeness of information provided by declarant.

- Medical and veterinary medicines for human and animal health,
- Food stuffs and food additives,
- Animal feedstuffs and feed additives,
- Special sweetener food additives,
- Cosmetics,
- The EU chemistry export / import control regulation,
- National legal regulations of member states.

This Regulation shouldn't apply to following [13];

- Radioactive substances,
- Non-isolated intermediates,
- Substances on their own in a mixture or in an article,
- The carriage of dangerous substances,
- Wastes (2006/12/EC),
- Exemptions for Defence by Member States
- Following substances are considered to be registered under the REACH [14];
- Plant Protection Products (91/414/EEC),
- Biocidal Products (Only active ingredients), (98/8/EC),
- Notifications according to 67/548/EEC (Only applies to the notifier).
- Following substances are exempted from registration and evaluation;
- The substances in annex IV and V under REACH Regulation [15].
- Polymers (Monomers are not excluded).
- The substances in their rules [16].
- The imported and exported substances from the European Union
- If imported substances already registered.
- Recovered substances already registered [17].

2.2.2.13. Application and evaluation under the REACH

Registering process of inventory before 1981 is divided into specific stages. These stages are yearly varied according to producing and using.

- There will not pre-registreted due to large data for “new chemicals” after 1981.
- After June 01, 2008 will be directly started registering process.
- It will not be fees for pre-registering by ECHA.
- In-phase substances are listed on EINECS.
- For substances producing or importing over 10 tonnes per year should be prepared a chemical safety report to including risk management tools.

2.2.2.14. Application and evaluation

The files under REACH will be evaluated as follows;

- Eligibility check: Qualification of information given by industry will be check by ECHA in Helsinki. It will be made through samples taken from registered files for each tonnage range (At least 5%).
- File evaluation: It will be given a proposal by the registrant for standard tests in animal experiments. This test proposal will be evaluated by ECHA to avoided to unnecessary animal experiments.
- The substance evaluation: It will be realized by the authorities in member states. All files will be examined in terms of information’s accuracy. This check is not for suitability or quality.

2.2.2.15. Stages for registrations [18]

Stages for registration under REACH will be evaluated as follows;

Stage 1: The last registration date are substances in November 30, 2010.

- The substances over 1000 tonne per year producing and importing in The European Union.
- The substances with CMRs over 1 tonne per year (carcinogenic, mutagenic or toxic substances).
- The substances with R50/53 risk code over 100 tonnes per year.

Stage 2: The last registration date are substances in May 31, 2013.

- For the substances between 100 tonnes and 1000 producing or importing in The European Union.

Stage 3: The last registration date are substances in May 31, 2018.

- For the substances between 1 tonne and 100 producing or importing in The European Union.

A. Registration [19]

Registrations are based on principles to "one substance, one registration".

Procuders and importers of the same substances are jointly obligated to submited to their registration.

Substances must be recorded to ECHA, otherwise, it will not be produced, used or sell in the European Union.

B. Who is responsible for pre-registration and registration of chemicals?

According to the REACH Regulations were introduced to some rules for responsibilities.

From pre-registrations and registrations of chemicals are responsible by representatives.

It can not be found on application by companies in non the EU for pre-registration and registration, but a legal person can be appointed as representative (only representative) by companies in borders of the EU.

C. Identification of the substances [20]

Identification of the substance as follows:

1. Name or other identifier of each substance

1.1. Name(s) in the IUPAC nomenclature or other international chemical name(s)

1.2. Other names (usual name, trade name, abbreviation)

1.3. EINECS or ELINCs number (if available and appropriate)

1.4. CAS name and CAS number (if available)

1.5. Other identity code (if available)

2. Information related to molecular and structural formula of each substance

2.1. Molecular and structural formula (including SMILES notation, if available)

2.2. Information on optical activity and typical ratio of (stereo) isomers (if applicable and appropriate)

2.3. Molecular weight or molecular weight range

3. Composition of each substance

3.1. Degree of purity (%)

3.2. Nature of impurities, including isomers and by-products

3.3. Percentage of (significant) main impurities

3.4. Nature and order of magnitude (… ppm, … %) of any additives (e.g. stabilising agents or inhibitors)

3.5. Spectral data (ultra-violet, infra-red, nuclear magnetic resonance or mass spectrum)

3.6. High-pressure liquid chromatogram, gas chromatogram

D. Evaluation [21]

All files in terms of compliance with registration obligations will be evaluated by ECHA. In addition, susceptible chemicals will be also evaluated by ECHA and by the responsible of members' countries. At the end of these evaluates can be decided authorisation or restriction or prohibition.

E. Authorisation [22]

It should be a separately license obtained by industry for trading and using of substances of very high concern (SVHC). These chemicals are:

- Substances with carcinogenic, mutagenic and toxic in category 1 and 2 (CMRs Cat. 1&2).
- Persistent, bio accumulative and toxic chemicals (PBTs).
- Very persistent and very bio accumulative (vPvB).

F. Restriction [23]

It can be decided on restricted for any substance with e special dangerous. Restrictions can be in various sizes. Substances in these situations can be all prohibits or they can be completely banned for the use of the public. Restrictions can be also applied to substances that do not required restriction.

2.2.2.16. Classification and labelling [24]

Having information about hazards and risk characteristic of chemicals is an important part of chemical safety. Labelling and classification as standard of dangerous goods were responsibilities of industries in previous legal regulations. There has a globally harmonised system of classification and labelling of chemicals (GHS) in new regulation.

2.3. Storage of dangerous substances

2.3.1. General

Safe storage of dangerous goods is an essential task for the health, safety and environment to reduce the risks relevant to the storage of packed dangerous substances. There are always risks of fire and explosion where hazardous materials are stored. Therefore, the operators and competent authorities must take all the precautions for safe storage. According to the US Chemical Safety Board, 46% accidents caused by hazardous chemicals occured because of improper storage conditions. The control of major accident hazards (COMAH) regulations are likely to be followed by the competent authorities to control establishments where dangerous substances are present above certain quantities. COMAH establishments are categorised as either “Upper-tier” or “Lower-tier” dependent on the nature and amount of chemicals or mixtures. Upper-tier or lower-tier establishments have to provide the basic necessary information to the corresponding competent authorities. Upper-tier establishments should provide more information. The aim of this training module is to discuss the basics of safe hazardous materials storage. Chemical storage facilities should meet certain standards well defined in European Union (EU) Industrial Safety Regulations which are also known as Seveso Directives. The majority of the provisions of Directive 2012/18/EU on the control of major accident hazards involving dangerous substances, known as the Seveso III are implemented by the COMAH Regulations 2015. The treshold quantities of dangerous substances that determine establishment whether classified in upper-tier or lower-tier category is given in Annex I in the Seveso III Directive. Let us give a brief information on how Seveso Directives came out. Major chemical accidents arised from industrial plants across the Europe from 1960s to 1970s became a growing concern in terms of major hazard potential for both the operators and local public. In July 1976, an industrial accident occured in a chemical plant of ICMESA company manufacturing pesticides and herbicides in a town, Seveso stands in north of Milano in the Lombardy region of Italy. The ICMESA trichlorophenol reactor released a toxic cloud containing tetrachlorodibenzoparadioxin (TCDD) which is known a poisonous and carcinogenic byproduct. Because of widespread contamination of the dioxin, 700 inhabitants of Seveso and other neighboring town Dema were evacuated from their homes. As a consequence of this tragic accident, European Union law, also known as Seveso I Directive (Directive 82/501/EC) on the control of major accident hazards of certain industrial activities, was adopted in 1982. Council Directive 96/82/EC on 9 December 1996 known as Seveso II Directive came into force across the member states upon a detailed review of Seveso I Directive in order to improve the safety of sites containing large amounts of dangerous substances. European Comission took the opportunity to modernise this directive and finally Seveso III (Directive 2012/18/EU) was adopted in 4 July 2002. The scope of Seveso III Directive is based on classification, Labelling and packing (CLP) of chemical substances and mixtures. Seveso III became a well organised Directive for the COMAH. Seveso III Directive basicly covers the issues: (a) identification of sites; (b) control measures to prevent major accidents; (c) mitigation measures to limit the effects of any accident which do occur.

2.3.2. Course objectives/identification

The aim of this module are as follows:

- To provide a knowledge about safe storage of dangerous substances,
- To minimize the risks, the hazard of fire, spillage from improper storage of dangerous substances
- To make the audience familiar with the types of containers and packagings used in storage of dangerous substances
- To reflect the points in designing warehouses for dangerous substances

2.3.3. Course outcomes

Several points can be given as the outcome such as:

- İncrease the concious among people dealing with storage facilities of dangerous substances in industry and other working areas
- Segregation and separation of chemicals are done according to the nature of the chemicals
- Perfect arangments of storage areas for dangerous substances
- Reducing the risk arising from improper storage facility

2.3.4. Classification

Dangerous substances should be assigned to the appropriate classes. Therefore, chemical substances are classified into three basic hazard categories for safe storage.

Physical hazards

- Fire (f.ex. flammable gas, flammable aerosols, flammabel liquids and solids)
- Explosion
- Sudden release of pressure (f.ex. puncture of high pressure tanks)
- Reactivity (fire, explosions or relezse of dangerous gases that can result from contact between particular chemicals and certain chemicals or air or water)

Health hazards

- A hazardous substance has potential harmful effect to health (f.ex. headache, skin burns results from contact with corrosive chemicals, exposure of certain chemicals may cause to organ damage, allergic-type reactions, cancer or death at further level)

Environment Hazards

- Certain chemicals exhibit hazard effects to water sources, soil or ozone layer.

2.3.5. Operation (how it is used)

This training module includes citation of legislations and operations about safe storage measures for dangerous substances in workplaces and warehuses as well. Having looked the chapter in detail, a test based training part (it was given at the end of this chapter) exists to evaluate how one gets the better ubderstanding of safe storage of dangerous substances.

2.3.6. Pros. and Cons.

2.3.6.1. Pros.

Dangerous substances can be separeted, segregated and stored according to the given SDS information supplied by the manufacturer in the correct manner by following the critical operation procedures carefully.

Classification system helps to store dangerous substances properly to ensure that the risk due to the improper storage of them.

2.3.6.2. Cons.

Since there are various number of dangerous substances or chemicals with different properties, it is not an easy task to categorize all them just by considering a few paramerters.

2.3.7. Identification of dangerous substances

Dangerous substance means a substance or mixture covered by Part 1 or listed in Part 2 of Annex I of the Directive 2012/18/EU of the European Parliment and the Council of 4 July 2012 on the control of major accident hazards involving dangerous substances, including in the form of a raw material, product, by-product, residue or intermediate.

2.3.8. Common hazards

A classification of certain chemicals of dangerous substances is needed for their compatibility and storage requirements. Hazard classifications include:

- Flammable solid
- Flammable liquid
- Flammable gas
- Toxic gases
- Dangerous when wet
- Organic peroxide
- Corrosive chemicals
- Spontaneously combustibles
- Oxidizing agents
- Toxic chemicals

2.3.9. Safety Data Sheets (SDS)

Safety Data Sheets (SDS) contains all the necessary information such as physical and chemical characteristics, fire and explosion hazard like flash point and flammable limits, reactivity and instability hazards, health hazard risks of the dangerous goods and substances, and required personal protective equipments (PPE) and meets the requrements set out in Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents stored in the warehouse. Therefore, it has been accepted an effective method for the safe handling and storage of dangeorus substancess. One can assure whether any chemicals possess any risk to the health or the environment just by looking the corresponding SDS. It also covers information about the requirements for storage. SDS of any dangerous substance must be prepared by competent person and specific details should be provided to the user by the supplier. In case of any revisions on SDS of a particular dangerous substance, users should be informed about the changes. A safety data sheet must be available for all dangerous goods in the warehouse to determine the following aspects for storage:

- Segregation requirements
- Personal protective equipment
- Fire extinguishing material
- Additional requirements for the construction of the building.

2.3.10. Placards and labelling

All the dangerous substances to be stored in the warehouse or storage area must be identifiable through their labelling on the container with at least their substance name. Dangerous substances and mixtures should be labeled. These labels or pictograms in accordance with legislation on hazardous substance indicate hazard presented by the substances during storage and transport.

Figure.2.32. Some common placards for hazard signs of chemicals for storage and transport.

Figure.2.33. A representative labelling on a container.

Dangerous substances must be clearly labeled or signed for the benefit of current users, warehouse owner/employer, emergency personnel, and future users [10].

2.3.11. Separation and segregation of dangerous substances

Incompatible dangerous goods must be segregated according to Safety Data sheets (SDS) requirements. All the hazardous properties of dangerous goods are given in SDS in order to have the hazard identification. SDS must be consulted for reactivity data to determine whether substances are incompatible. Thus, chemicals can be segregated by hazard class. Do not store chemicals alphabetically unless they are compatible. The segregation of dangerous substances must be performed based on the hazardous materials compatibility charts as given in Table 2.50. Separation of dangerous substances are generally achieved by positioning of different groups in separate areas within a store or warehouse. Segregation on the other hand is done placing dangerous substances in separate storage areas or by physical barriers or walls whitin a certain storage area. If flammable dangerous substances are of the concern, barriers should have to be fire resistant. Segregation of dangerous substances provides advantage of reducing any risks that would occur due to mixing of incompatible chemicals. A general recommendation for the segregation of dangerous substances according to their hazard classification is given in Table 2.50.

Table.2.50. Segregation chart for incompatible dangerous substances.

Table 1

The table shows general recommendations for the separation or segregation of different classes of dangerous substances

		CLASS	2			3	4			5		6	8
	CLASS												
COMPRESSED GASSES 2.1 Flammable	2			KEEP APART	Segregate from OR KEEP APART	Segregate from	Segregate from	Segregate from	Segregate from	Segregate from	ISOLATE	KEEP APART	KEEP APART
2.2 Non-flammable/non-toxic			KEEP APART		KEEP APART	KEEP APART	Separation may not be necessary	Segregate from	Separation may not be necessary	Separation may not be necessary	Segregate from	Separation may not be necessary	KEEP APART
2.3 Toxic			Segregate from OR KEEP APART	KEEP APART		Segregate from	KEEP APART	Segregate from	KEEP APART	Separation may not be necessary	Segregate from	Separation may not be necessary	KEEP APART
FLAMMABLE LIQUIDS	3		Segregate from	KEEP APART	Segregate from		KEEP APART	Segregate from	Segregate from	Segregate from	ISOLATE	KEEP APART	KEEP APART
FLAMMABLE SOLIDS 4.1 Readily combustible	4		Segregate from	Separation may not be necessary	KEEP APART	KEEP APART		KEEP APART	Segregate from	Segregate from	Segregate from	KEEP APART	Separation may not be necessary
4.2 Spontaneously combustible			Segregate from	Segregate from	Segregate from	Segregate from	KEEP APART		KEEP APART	Segregate from	ISOLATE	KEEP APART	KEEP APART
4.3 Dangerous when wet			Segregate from	Separation may not be necessary	KEEP APART	Segregate from	Segregate from	KEEP APART		KEEP APART	Segregate from	Separation may not be necessary	Separation may not be necessary
OXIDISING SUBSTANCES 5.1 Oxidising Substances	5		Segregate from	Separation may not be necessary	Separation may not be necessary	Segregate from	Segregate from	Segregate from	KEEP APART		Segregate from	KEEP APART	KEEP APART

Most of the chemicals possess different hazards. The areas where the chemical substances are stored can be determined by knowing the harmful properties of these substances and by assessing the consequencies of any accident occured within the storage areas. This can be seen with different examples. For example, if a chemical is flammable and corrosive, it would be appropriate to store the chemical together with other flammable substances.

- Acetic acid is both an abrasive acid and a flammable liquid. It should be stored away from corrosive bases such as sodium hydroxide and oxidizing acids such as nitric acid.
- If hydrochloric acid somehow contacts with ironfillings they produce hydrogen gas, a flammable gas, which may cause fire or explosions. Therefore, they should be kept apart from each other by a distance or a barrier. If for example, flammable substances are of concern, the barrier should be expected to be fire resistant.

However, if a chemical is both flammable and highly toxic, other factors must be taken into account before choosing the appropriate storage area, such as the physical properties of the chemical and the amount stored.

- Phenol is flammable, toxic and corrosive. It should be stored according to most likely hazard found in the warehouse. If contamination risk exists in the storage area then, it should be kept away from oxidisers like nitric acid.

There will always be some chemicals that will not fit in a categorical or other place, but when the release of an accident where chemical hazards are correctly identified by using information available in the SDS, most chemicals must be assigned to suitable storage areas and all storage rules must be obeyed. The more common chemical substances that should be kept away from each other are listed in the Table 2.51.

Table.2.51. Some most common incompatible chemicals [12-13].

Chemicals	**Incompatible with**
Acetic Acid	Chromic acid, nitric acid hydroxyl compounds, ethylene, glycol, perchloric acid, peroxides, permanganates
Acetone	Concentrated nitric and sulfuric acid mixtures
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury

Alkali Metals, like calcium, sodium potassium	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, the halogens
Ammonia, anhydrous	Mercury, chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid
Ammonium Nitrate	Acids, metal powders, flammable liquids, chlorates, nitrites, sulfur, finely divided organic or combustible materials
Aniline	Nitric acid, hydrogen peroxide
Arsenical materials	Any reducing agent
Azides	Acids
Bromine	Same as chlorine
Calcium	Oxide Water
Carbon (activated)	Calcium hypochlorite, all oxidizing agents.
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, metal powders, sulfur, finely divided organic or combustible materials
Chromic Acid	Acetic acid, naphthalene, camphor, glycerin, turpentine, alcohol, flammable liquids in general
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, turpentine, benzene, finely divided metals
Chlorine Dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Copper	Acetylene, hydrogen peroxide
Cumene Hydroperoxide	Acids, organic or inorganic
Cyanides	Acid
Flammable Liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Hydrocarbons	Fluorine, chlorine, bromine, chromic acid, sodium peroxide

Hydrocyanic Acid	Nitric acid, alkali
Hydrofluoric Acid	Ammonia, aqueous or anhydrous
Hydrogen Peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, flammable liquids, oxidizing gases
Hydrogen Sulfide	Fuming nitric acid, oxidizing gases, acetylene, ammonia (aqueous or anhydrous), hydrogen
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Sulfuric acid
Nitric Acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases
Nitrites	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic Acid	Silver, mercury
Oxygen	Oils, grease, hydrogen; flammable liquids, solids, or gases
Perchloric Acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosphorus (white)	Air, oxygen, alkalis, reducing agents
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium Chlorate	Sulfuric and other acids
Potassium Permanganate	Glycerin, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds
Sodium	Carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts

Sodium Peroxide	Ethyl or methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerin, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulfides	Acids
Sulfuric Acid	Potassium chlorate, potassium perchlorate, potassium permanganate (or compounds with similar light metals, such as sodium, lithium, etc.)
Tellurides	Reducing agents

2.3.12. Packaging and containers

Dangerous substances manufacturers or first suppliers have to ensure that the dangerous substances are packed according to the corresponding ADR regulations before supplying them to any consumer. Packing and containers are therefore the primary protective measures while storing and transporting those substances. Combustible liquids or substances too dangerous to be transported must be packed in packagings and containers, which are made of metal or particular materials with emergiency vents, in a condition that will retain the liquids and will not react with the materials inside.

There are several requirements for appropriate packings for the transport and storage of dangerous substances. These are as follows [2-10].

- Packings should be made of the most appropriate material and must possess enough strength to shocks, handling or stacking loads, vibrations, temperature changes, moisture or pressure changes under transport or storage conditions. Any failure of these requirements for packings will not be suitable for the transportation and storage of dangerous substances.

Figure.2.34. Stacks of dangerous substances in packings in a warehouse.

- Packaging containers, their lids and other equipments should be manufactured from inert materials that do not interact chemically with the dangerous substances which they hold in.
- Dangerous substances should be kept in adequet packages on which appropriate labelling is done related to package content.
- Outer packaging is somethimes required and all the necessary information on the cardboard box is provided by the manufacturer or first supplier.
- Internal packagings such as glass bottles or plastic containers are put in cardboard boxes so as to avoid any damage that can occur during transport as a result of load or pressure. Protection against physical damages can be achieved with soft materials used in outer packaging.
- Only same class of dangerous substances should be packed together, otherwise they should be in separate containers to avoid any reaction forming unstable substances.
- All the packaging openings should be fitted with a secure and well-fitting cap or lid that resist the escape of flammable liquid or vapours, even if the container falls or rolls over.
- Packagings should have a proper shape and dimensions for a safe transportation and storage facility [10].

The choice of the correct packagins is strongly depends on type and amount of the chemical, size and the need for stregth. Some of the containers are made of plastic and some of them are made of steel material. The opening way of the packagings can be one of the choice reason as well [9].

- Tigth head plastic drums of different sizes are preferred generally for industrial solvents such as ethanol or acetone. Open head plastic drums on the other hand are more approriate for solid (powder, crystal, etc.) dangerous substances. Since their opening lids are not leak proof they are not suitable for liquid substances.

Figure.2.35. Examples of various shapes and sizes of plastic containers.

- Steel drums are used to store liquid dangerous substances (diethyl ether, chloroform, etc.) that are not suitable to be stored in plastic containers. These type of containers are not suitable for acids. It is obvious that acids will react with steel material and may weaken the strength of the container.

Figure.2.36. Drums made of steel.

These types of drums can have either a tight head or open head opening lid. Open head steel drums provide advantages for keeping solid substances as well as inner packagings. However, open head drums are not appropriate for liquid dangerous substances since their lids are not leak proof [18].

Figure.2.37. Improper storage of liquid substances may cause leakage from open head drums.

- Apart from those steel and plastic drums, there are also a composite form of drums which are more durable and whose inside layer is plastic, polyethylene, whereas outside coating is steel to improve stregth for external factors. These type of packagings offer to keep a wide variety of different chemical solvents.

- Intermediate bulk containers (IBCs) are very common containers for both liquid chemicals and waste dangerous substances as well. They have bigger storing volumes compared to drums. They may be made of different materials such as metal, composite (metal outside coating and plastic inner coating) and plastic.

Figure.2.38. Stacks of Intermediate bulk containers (IBCs) in a storage building.

2.3.13. Location and design of storage area

The general rules for the location, design of storage areas as well as storage of dangerous substances deserve considerable attention in order to reduce the potential risks that dangerous substances carry. Specific standards regarding to safe storage of especially oxygen, hydrogen, acetylene, anhydrous ammonia, nitrous oxide, etc. should be followed for the storage facilities. These substances may require specific requirements like firewalls to kept them separate in side the storage area with in the building.

2.3.13.1. Location

Areas where hazardous materials are stored should be located away from places where the population is dense, from sources of drinking water, from areas where flood hazards can occur. Transportation and emergency services should be easily accessible in chemical storage areas. Electricity, fire fighting water etc. should be provided [8].

2.3.13.2. Security

In order to reduce the risks that may arise in the areas or locations where dangerous goods are stored, only authorized personnel should be allowed to access the area and permission for unauthorized actions should not be allowed.

Given the potential risks, security systems procedures should be developed to ensure the safety of employees in such locations, the control of access from residential areas and roads and likelyhood of mischief or sabotage [19].

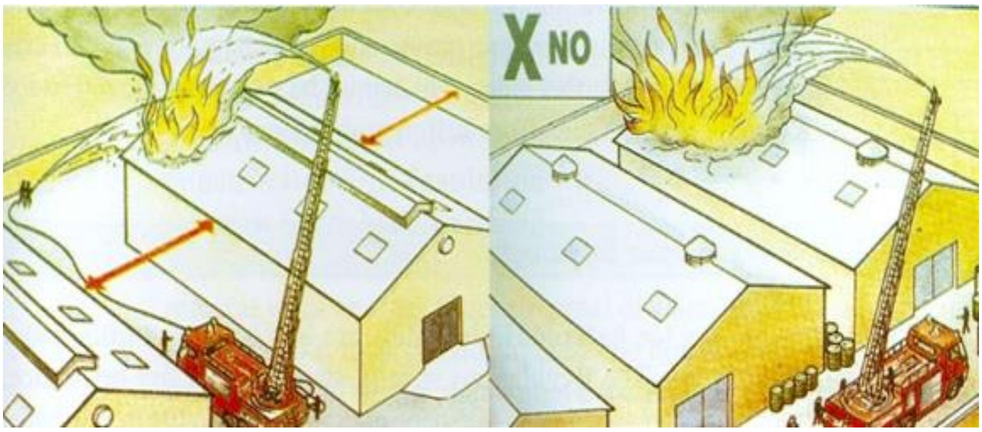
For security reasons, there is a need for a system that monitors the entry and exit of authorized persons who are allowed access to the areas where hazardous materials are stored.

Security level storage includes locks to keep doors, windows, entrances to the building closed, security checks for vehicles entering and exiting the area, and restrictions on non-workers entering and exiting certain locations.

2.3.13.3. Site layout [8-20]

The site layout should be designed so that incompatible dangerous materials are stored at different locations by using separate buildings, fire walls or other measures. It should provide safe movement and transportation of hazardous materials and offer sufficient working areas and access from two sides.

Figure.2.39. Separation of wharehouse buildings from each other.



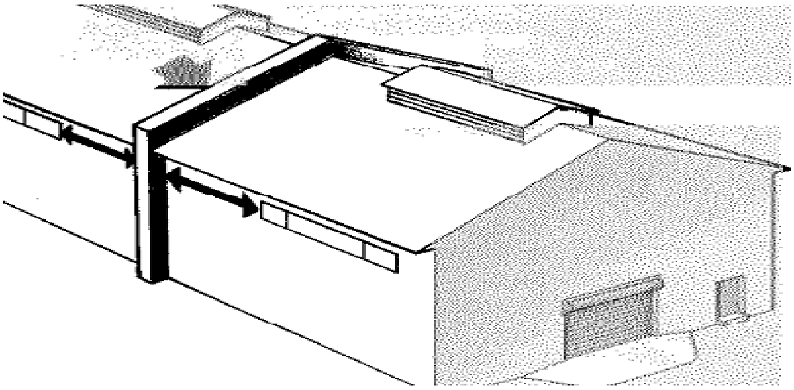
2.3.14. Design of warehouse buildings

The layout where hazardous chemicals are stored must be designed to have emergency exit doors, taking into account the hazard characteristics of the materials. The warehouse must be built as compartments to separate or segregate incompatible hazarodus materials. There shouldn’t be office, technician room etc. within the warehouse. Where there are such places needed, it must be able to withstand at least 60 minutes against the fire.

2.3.14.1. Walls

External walls can be covered with steel or similar coatings If there is no risk of fire. However, if there is a risk of fire from the outside, the external walls need to be reinforced. Insulation materials to be used on the walls of buildings must be non-combustable like mineral wool or glass fiber. The walls used in the interior of the buildings to act as fire breaks, must be resistant to fire for at least 60 minutes and should rise to a height one meter above the roof. This would prevent a fire from spreading into the different compartments [20].

Figure.2.40. Interior fire wall design for a safe warehousing facility.



Concrete, brick and concrete blocks are the most prominent materials in terms of fire resistance in other materials. Concrete walls should be at least 15 cm thick and bricks must be at least 23 cm thick for the desired strength. Hollow bricks are not suitable for this operation. The thickness of unreinforced concrete blocks must be at least 30 cm to ensure requisite strength and stability. For a better structural strength on the walls, reinforcing columns in the fire walls are recommended. The pipes and electic cables passing through the fire walls must be placed in fire resistant sand cups.

2.3.14.2. Fire doors

The existing doors in the warehouse must be fire resistant, just as the walls. The doors must be integrated into the fire detection system and, in the event of a fire, must be able to be closed automatically or via a fusible link. Anything that would prevent the doors from being closed in case of an emergency should be avoided.

2.3.14.3. Emergency exits

Emergency exits should be positioned so that there are at least two on each floor. Where these doors are to be placed in the storage area should be carefully determined and they should be placed in appropriate locations so that in case of an emergency no one is confined inside. There should be emergency exit warning signs showing in which directions the exits are. The doors must be fitted in such a way as to open from the room, passage or staircase, and should not be locked or fastened and should be free from obstructions. They must be easy to open in the dark.

2.3.14.4. Floors

The floor must be sufficiently strong and resistant to the applied load. The basement structure must be resistant to collapse, abrasion and punctures from liquid chemicals stored. The floors should be smooth as possible, but not slippery. Floors should be designed as to contain leakage and contaminated fire-fighting water, for example by means of a surrounding sill or curb. The sills should hold a volume which is at least 110 % of the largest capacity container. Ramps may need to be provided to allow the passage of vehicles such as forklift-trucks, wheeled trolleys or pallet-trucks to the storage area.

Figure.2.41. Forklif trucks should move easily on the floor inside the storage area.

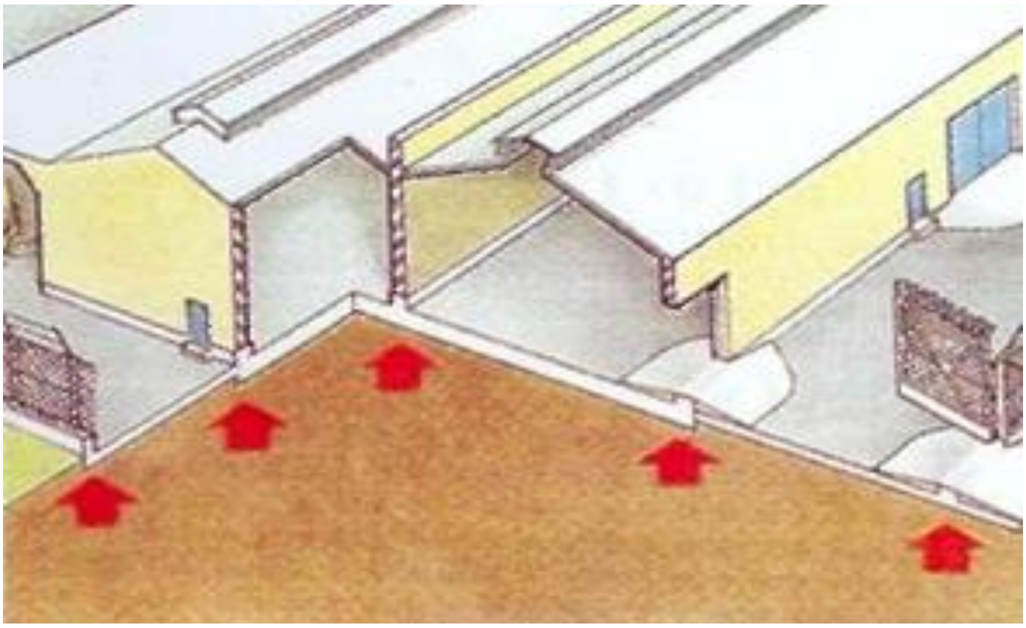
2.3.14.5. Drainage system

There is a need for a drainage system for the warehouse in order to drain rainwater from roof and as well as outside. The drainage system is important in terms of uncontrolled release of fire-fighting water and prevention of spilled or released chemicals. Impervious sills should be installed to prevent uncontrolled spillages in outdoor storage areas. The floor of the storage area must be impervious and sloped so that dangerous materials spilled can accumulate in a controlled area. According to the characteristics of the chemicals stored in the warehouses, any dangerous liquid spilt from the containers can be retained where spillage occurs by placing an interceptor pit in the drainage system.

2.3.14.6. Bunding

In the warehouse, there should be bunds to contain any spilt liquid and sills to prevent its spread through the doors. These bunds should be impervious and resistant towards dangerous chemicals. Where spillage of liquid chemicals is high, there should be a seperate drainage system with a sloped floor, bund, a containing a collection sump [8].

Figure.2.42. Design of bunds in the storage area.



2.3.14.7. Roof

The roof should not allow rainwater to flow in and should be so that smoke and heat can be released in the event of a fire. There is no special construction material requirement for the roof, but materials that can cause fire such as wood should be avoided. The frames of the roof can be made of hard or treated wood, but the external covering must be made of non-combustible material. The roofing material should be light and friable as well so that it would fall down in case of a fire and will provide smoke and heat can come out. The roof must have transparent ventilation panels and these panels must be kept open, can be opened easily and or must be automatically opened in case of a fire. Early release of smoke and heat through those openings will help to respond and prevent spreading of the fire.

2.3.14.8. Ventilation

Warehouse should be adequately ventilated to disperse vapor from any leakage or spillage taking into account that hazardous gases and liquids can reach to levels low flammability limits or concentrations dangerous to health. Ventilation can be done mechanically or through the pannels on the roof [14].

2.3.14.9. Lighting and electrical equipment

Activities such as welding, battery charging should be done under well ventilated storage areas or somewhere outsite the warehouse. Necessary precautions should be followed prior to those kind of operations if they have to be done inside the warehouse.

Storage facilities are carried out during daytime only and it is better not to use any artificial ligthining source. In order to reduce the need for electrical lines, transparent panels can help to supply more light from outside. In case lighting and other facilities are needed, all the electrical equipments and cables should be installed according to meet standards, by a qualified technician.

All electrical equipment must be positioned away so as to avoid damages by forklift-trucks or pallets or water contact. They must be earth grounded and equipped with a overload protection system.

If there are dangerous chemicals having low flash point or fine dust liable to explosion, flame proofed wiring cables and equipments such as froklift-truck should be used. All of them is dependent on the property of the chemicals, theri flash points and the quality of the ventilation system as well. Required precautions should be followed according to information supplied from the supplier.

Activities such as welding, battery charging should be done under well ventilated storage areas or somewhere outsite the warehouse. Necessary precautions should be followed prior to those kind of operations if they have to be done inside the warehouse.

2.3.14.10. Heating

Heating of storage areas is generally not preferred to avoid ignition, but indirect heating methods such as steam, hot water, warm air should be preferred if the stored materials need to be heated against freezing, and the heating sources should be deployed outside the warehouse. Electrical heating systems should not be preferred, and mineral wool, glass fiber or nonflammable materials should be used to insulate the building and to keep the storage area warm.

2.3.14.11. Outdoor storage

Particular dangerous substances may need to be stored outside rather than in warehouse under the condition that such storage conditions does not contradict with the storage conditions specified in the SDS. Outdoor storage areas must be secured, and all stored substances must be covered with flame-retardant materials. In that case, the location area should be surrounded by bunds to contain the liquid as it is done inside the warehouse. The upper part must be covered with roofs, sunblinds or tinted window glass to protect against rain water and sunlight and UV radiation. However, this process may possess some problems:

- Stored materials must be kept above the floor on pallets or in containers in order to prevent being damaged by water [15].

Figure.2.43. Stacks of different size drums above the floor level.

- Chemicals stored outside can be exposed to high temperatures, which can cause a chemical degradation. For this reason, the material safety sheets of the chemicals stored outside must be carefully examined.
- The ground for the chemicals to be stored outside must be made of heat and waterproof impervious material so that the ground water and soil are not contaminated. Asphalt should not be preferred because in hot climate, the asphalt softens.
- The area enclosed by the bunds must be equipped with drainage system controlled with a valve.

- Outdoor storage utilizes weatherproof drums of 200 liter capacity which are used to store chemicals that are not sensitive to higher temperatures.
- Drums should be placed above the pallets on the ground.
- The chemicals stored in the open storage area should be closely controlled so that they do not cause a leakage that would pollute the drainage system.
- Empty drums or containers and expired dangerous chemicals must be stacked in a separate, designated area, and the area must be labeled as “Quarantine Area” or “Expired Chemicals” [15].

Figure.2.44. Empty or waste drums collected in a designated area.

There is a need for a racking system to store the drums over the top. The racks should be made by authorized personnel to ensure proper storage.

Figure.2.45. Drums are stacked on top of each other with a racking system.

Damage to racking that may occur as a result of forklift truck should be controlled periodically and repaired immediately. The hazardous materials storage area must only be dedicated to storing hazardous substances. Stored dangerous substances must be stacked carefully to minimize the risk of causing any damage. The height of the stacks must not rise up to the ceiling in building storage. Actually, there should be a minimum of about 90 cm space between the top of the stacks and the ceiling [15].

If stacks of drums are stacked without using racking, then the maximum stack height in safe limits should be determined taking into account the packaging load-bearing capacity [18]. Outdoor storage is highly recommended for drums containing certain types of materials such as highly flammable liquids, gas cylinders, or liquid chlorine.

2.3.15. Safety rules for dangerous substances

Safety is an important task for the handling, use, transportation and storage of hazardous materials. All necessary safety measures should be taken into account because hazardous materials are still dangerous in any case. All the actions regarding the safe management of the materials can prevent us from emergencies. Special requirements to ensure a safe working condition are certainly vital. They are systematically argued and repeated in the many sections in this training module. Certain type of safety rules regarding to different types of dangerous goods are already cited under the correspondig titles. Moreover, some of very basic rules are listed below.

- All employes dealing with dangerous substances should be trained on how to handle, use, store, and dispose those substances. They should follow the procedures while working.
- Appopriate personal protective equipments (PPEs) should be used and damaged or torn PPEs should be discarded to avoid any injuries.
- Make sure what type of dangerous goods you are working with. Refer to SDS data label on the container to identify the hazards and the precautions you will take. Never use unlabeled containers, dispose them according to the specified procedures. If you are unfamiliar with a particular dangerous substance, then contact supplier for detailed or additional information.
- Inspect the containers of the chemicals whether they are damaged or they keep their form as they should be.
- Touching, smelling, or tasting is absolutely forbidden to understand the hazard of the dangerous goods.

- Never eat or drink somethink while dealing with dangerous substances. If you think that your hands are contaminated follow the precaution procedures given in the SDS.
- Store all the materials accourding to specified storage procedures after you finished your work.
- Distinct hazards of the substances should be clarified and local hospitals, fire departments and any other competent authorities in the field should be informed before. In case of an emergiency, the procedures tought in the training should be followed and the appropriate PPE should be used. The cause of the emergency shuld be reported as well.
- Fire extinguishers, eye wash stations, and showers, at certain locations should be available. Kitchen and dressing rooms must be located separate away from the storage area by at least 10 m.

2.3.16. Explosives

An explosive substance or mixture; is a solid or liquid substance or mixture of substances that may cause spontaneous chemical reaction to produce gas at temperature, pressure and velocity which will damage the environment. Pyrotechnic materials are also included in this definition, even they do not form gas. Explosive chemicals can produce a huge amounts of destructive energy which in turn may cause deaths, serious injury and severe damages.

2.3.16.1. Storage [1-9]

- A special area for storing and using explosive materials must be established.
- The storage rooms must be well built and securely locked when not in use.
- Storage areas should be located far away from other buildings and structures in order to minimize any damage that may result from any explosion
- Storage area should be well ventilated and free from moisture
- Natural lighting or portable electric lamps should be used or lighting outside of the storehouse.
- Natural lighting or portable electric lamps should be used in the warehouse or lighting should be done from outside.
- The warehouse floor must be made of timber or any other material that does not create sparks.

- The area around the storage area should be free of hay, garbage and other combustible materials
- No warehouse should be near oil, oil, flammable or combustible waste, open fire or flaming buildings.
- Persons using explosive materials should be trained in safe storage methods, such as the hazards of chemicals
- The presence of explosive peroxide-forming products in liquid containers should not be allowed during storage.
- Black powder and explosives should be stored in separate storage areas.
- There should be no tools, explosives or any other materials in the storage area.
- Stainless tools should be used to open the boxes of explosives.

2.3.17. Flammable gases

Flammable gas is a gas or gas mixture having a flammability range of 101.3 kPa at standard pressure and a temperature of 20°C.

2.3.17.1. Storage

- Flammable gases should be kept away from sunlight, all sources ignition: heat, flame or sparks.
- The walls, ceilings and floors of the storage rooms must be made of durable materials which are fire resistant for at least two hours.
- Storage rooms should be fitted with automatic closing fire doors.
- Installation of storage rooms should be electrically grounded and periodically checked or automatic smoke or fire detectors must be installed.
- Flammable substances should be stored in cool and well ventilated places to avoid accidental formation of airborne vapors and contamination.
- Vapors of flameproof solvents may be heavier than air and may travel past the source of distant ignition. Flammable vapors of spilled chemicals can descend from the stairwells and elevator cavities and burn down in the lower floors. Therefore, the use of cigarettes and open flames should be prohibited where these solvents are used and stored.
- 'Non-smoking' signs must be visible on the areas where flammable materials are stored.

- The safest way to store flammable materials is to use portable and approved safety containers. Flammable materials are usually transported using 200 liter cylinders, but these should not be considered for long term storage.
- The lid of the storage cabinet must be carefully removed and replaced with an approved pressure relief outlet to prevent an increase in internal pressure which may result from exposure to heat, fire or sunlight.
- Very readily flammable materials should be kept separate from strong oxidizers and spontaneously flammable substances.
- A fire extinguisher suitable for the hazard of chemical substance must be kept in the ready condition and the necessary training should be given to those who will use it.
- When flammable materials are transferred from metal materials, a working closed transfer system must be used or suitable exhaust ventilation must be provided.

2.3.18. Flammable aeresols

Aerosols are colloidal systems formed by the dispersion of small solid or liquid particles in gas or liquid. Aerosols are biphasic systems in which the internal phase is liquid or solid other phase gas. They are placed in aerosol containers irrespective of their internal phase. Aerosol containers contain a compressed, liquefied or pressurized dissolved gas, which acts as a driving force in the delivery of aerosol.

In other words, in aerosol containers, Foam, paste or powder, or in the form of liquid phase in the form of solid or liquid particles in a gas. These containers can be metal, glass or plastic.

2.3.18.1 Storage

- Aerosol containers should be placed separately and alone, as low as possible.
- It should be stored in a storage or trailer built in a separate place outside the building and away from the building.
- If outside storage is not feasible, it should be stored indoors, away from sources of ignition, in accordance with one of the following: (a) In a separate room, (b) In metal cupboards, (c) In wire mesh cages.
- It must be protected from sunlight. It should not be exposed to temperatures exceeding 50°C.

- Flammable materials should be stored in cool enough places to avoid accidental formation of airborne vapors.
- Vapors of flameproof solvents may be heavier than air and may travel past the source of distant ignition. Flammable vapors of spilled chemicals can descend from the stairwells and elevator cavities and burn down in the lower floors. Therefore, where these solvents are used and stored, the use of cigarettes and flames should be forbidden.
- The safest way to store flammable materials is to use portable, approved safety containers. 200 liter cylinders are usually used for transporting flammable materials but they should not be considered for long term storage.
- The lid of the storage cabinet must be carefully removed and replaced with an approved pressure relief outlet to prevent an increase in internal pressure which may result from exposure to heat, fire or sunlight.
- When flammable materials are transferred from metal, they must use the working closed transfer system or have suitable exhaust ventilation.
- Very readily flammable substances must be separated from strong oxidizers and spontaneously flammable substances.
- In case of emergency, fire-fighting equipment and absorbent inert materials such as dry sand and earth should be provided.
- The walls, ceilings and floors of the storage rooms must be made of materials resistant to fire for at least two hours.
- Storage rooms should be fitted with automatic closing fire doors.
- Electrical installations of storage rooms should be grounded and periodically checked or automatic smoke or fire detectors should be installed in the storage rooms.

2.3.18. Oxidizing gases

The oxidizing gas is any gas or gas mixture that gives oxygen or contributes more to the combustion of other materials than air.

2.3.18.1. Storage

- The storage area should be cool, well ventilated and fire resistant.
- Flammable materials should be kept away from areas where oxidizing materials are stored.

- Some oxygen donors emit oxygen at the temperature of the storage room, while others require heat for this. If the containers of the oxidizing materials are damaged, the contents may mix with other flammable materials and may cause fire. This can be avoided by storing the oxidizing agents in separate storage areas. But this may not always be feasible.
- Strong oxidizing agents should not be stored next to flammable liquids as they have a low flash point.

2.3.19. Gases under pressure

Pressurized gases are liquefied or liquefied and cooled gases held in a chamber at a pressure of 200 kPa or more. They consist of compressed gases, liquefied gases, dissolved gases and cooled liquefied gases. Compressed gases can release high pressure or may explode.

The critical temperature is the temperature at which a pure gas can not be liquefied when it goes up, regardless of the degree of compaction.

Gases under pressure are classified into four groups according to their physical condition:

- Compressed gas
- Liquefied gas
- Refrigerated liquefied gas
- Dissolved gas

2.3.19.1. Storage [2-10-12-19]

- The warehouse should be single-storey, preferably fireproof, ceilings made of light and nonflammable material.
- The cylinders should be separated according to the nature of the gas contained in the cylinders and stored in separate fire-resistant buildings or sections.
- The cylinders must be kept together.

Figure.2.46. Gas cylinders are fixed in safe cabinets.

- Gas cylinders should be inspected whether they are in good pysical condition, free of cut, gouge and fire damage. Cylinders with bulged-cylinder Wall, sprains and strains, falls, bruises or broken bones should never be used.
- Never move the cylinders by draging or sliding. Use appropriate hand trucks to carry them.

Figure.2.47. A typical gas cylinder hand truck.

- Never drop or strike them to each other.
- You should not use the gas cylinders as the rollers to carry or move something.
- Never lift them from their cap of via magnets.
- It is not recommended to move the cylinder with valve and pressure regulator attached or with the valve open.
- The places where the cylinders are stored must have proper ventilation and doors to the capacity of the warehouses [2].
- The tanks must be dry so that the cylinders are not exposed to corrosion. Gas cylinders should be stored away from salt, corrosive substances, smoke, heat sources.
- Storage should not be made in direct sunlight areas.

- Storage under the floor should not be done.
- Filled and empty cylinders must be stored separately.
- The temperature of the storage area should not exceed 65°C.
- Gas cylinders must be stored away from easily combustible materials such as petroleum products and corrosive substances.
- Storage areas should be easy to see warning labels according to gas type.
- Cylinders should be stored in such a way that they are not subject to chemical effects such as corrosion and mechanical effects such as impact, drop, cut.
- Passages and emergency exits should not be closed during storage of the cylinders.
- The tube must be fixed with a chain or belt so that the rollers do not tip over by impacts such as collision or stabbing [15].

2.3.20. Gas cylinders for flammable gases

Flammable gases should be stored away from open flame sources, heat sources, oxidants.

In areas where these gases are stored, grounded outlets and explosion-proof electrical equipment should be used.

Sufficient number of fire extinguishers must be provided for emergency response in the storage area.

"No smoking" signs shall be affixed to the perimeter and entrance of the storage area.

Flame sources should not be used to detect gas leaks. For this purpose, a gas detector or appropriate leak detection solutions should be used [15].

2.3.21. Gas cylinders for high grade oxidizing gases

High-temperature oxidizing gas cylinders should be stored away from flammable gas cylinders and flammable materials.

Valves, regulators and pipe fittings used in oxygen cylinders must be made of oxygen-compatible materials.

2.3.22. Gas cylinders for noble gases

Respiratory devices should be used in areas where the amount of oxygen is low.

Some gases or vapors may cause death if inhaled. Therefore, the storage areas should be well ventilated since inert gases are stifling.

Where there is a gas leak in the prime gas storage areas, trained personnel should interfere with the leak by wearing a breathing apparatus. The environment should be thoroughly ventilated after the leak has ceased [15].

2.3.23. Gas cylinders for corrosive, toxic or very toxic gases

Personnel working in the areas where these gases are stored should be trained on the hazards of the gases.

Questions regarding the storage of these gases are not checked for safety information provided by the gas supplier and must be communicated to the gas supplier when necessary. Corrosive dangerous substances can cause skin or eye burns or damage other stuffs in the storage area. Emergency eye shower and emergency body shower should be kept in the storage area [15].

2.3.24. Gas mixtures

Gas cylinders should be identifiable Information about gas mixtures should be included. Precautions should be taken to ensure that the gas contained in the gas mixture in storage is in accordance with the hazard class [15].

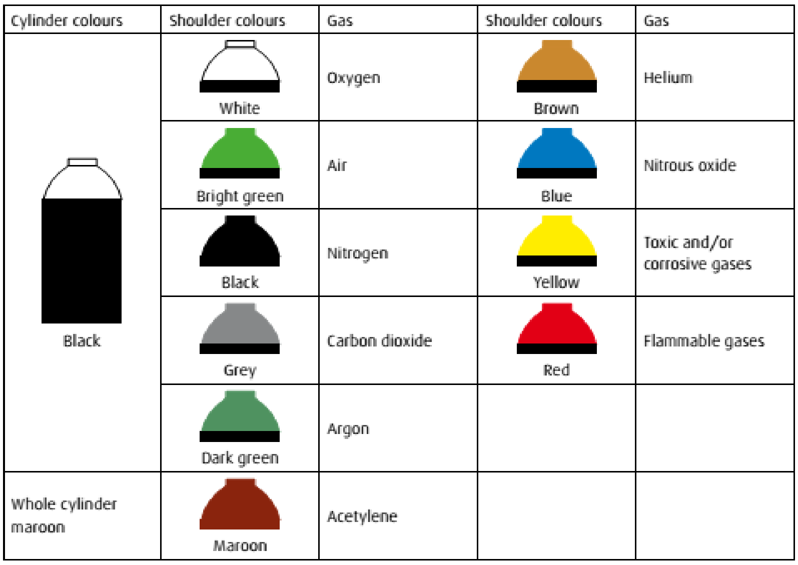
Table.52. Colors of gas cylinders and corresponding hazard class.

General Colors	Hazard Class
Red	Flammable
Yellow	Toxic or corrosive
Light blue	Oxidising
Bright green	Inert
Red and yellow	Flammable and toxic
Yellow and light blue	Toxic and oxidising

Colored according to this standard in order to avoid possible confusion.

Figure.2.48. Gas cylinders colors for different kinds of gases and their mixtures.

Figure.2.49. Gas cylinders color coding for some more common industrial gases.



Cylinder colours	Shoulder colours	Gas	Shoulder colours	Gas
Black	White	Oxygen	Brown	Helium
	Bright green	Air	Blue	Nitrous oxide
	Black	Nitrogen	Yellow	Toxic and/or corrosive gases
	Grey	Carbon dioxide	Red	Flammable gases
	Dark green	Argon		
Whole cylinder maroon	Maroon	Acetylene		

- Please note that although gas cylinders are classified according to the color coding fort he identification, this might not be reliable always because colors of the gas cylinder for a particular gas may be vary with the supplier.

2.3.25. Flammable liquids

Flammable liquids are liquids with a flash point below 60°C.

Flammable liquids are classified into three categories:

Category 1: Flash point <23°C and initial boiling point < 35°C

Category 2: Flash point <23°C and initial boiling point > 35°C

Category 3: Flash point > 23°C and < 60°C

Category 4: Flash point > 60°C and < 93°C

2.3.25.1. Storage

- Flammable materials should be stored in cool enough places to avoid accidental formation of airborne vapors.
- Flammable materials must be stored in a well-ventilated area.
- Vapors of flameproof solvents may be heavier than air and may travel past the source of distant ignition. Flammable vapors of spilled chemicals can descend from the stairwells and elevator cavities and burn down in the lower floors. Therefore, the use of cigarettes and open flames should be prohibited where these solvents are used and stored.
- The safest way to store flammable materials is to use portable, approved safety containers. Flammable liquids of more than 1 liter should be stored in metal cups. Flammable materials are usually transported using 200 liter cylinders, but these should not be considered for long term storage. Storage cabinet
- The lid must be carefully removed and replaced with an approved pressure relief outlet to prevent internal pressure build-up from exposure to heat, fire or sunlight.
- When flammable materials are transferred from metal materials, a working closed transfer system must be used or suitable exhaust ventilation must be provided.
- Very readily flammable substances must be separated from strong oxidizers and spontaneously flammable substances.
- The electric lamp used in the place where very volatile liquids are stored must be approved as non-flammable and must not be allowed to open in or near the storage area.
- In case of emergency, fire-fighting equipment and absorbent inert materials such as dry sand and earth should be provided.
- The walls, ceilings and floors of the storage rooms must be made of materials resistant to fire for at least two hours.
- Storage rooms should be fitted with automatic closing fire doors.
- Electrical installations of storage rooms should be grounded and periodically checked or automatic smoke or fire detectors should be installed in the storage rooms.
- Control valves on storage tanks containing flammable liquids must be clearly marked and pipelines should be painted with different safety colors to indicate the liquid type and flow direction.

- Flammable or combustible liquids can catch fire or explode. Therefore, the tanks containing flammable substances must be placed so as to extend downward from the main premises and factory premises.
- If they are on a flat surface, sufficient clearance must be left to prevent fire spread and ditches must be made. The trench capacity should preferably be 1.5 times the storage tank, despite the possibility of flammable liquid overflow. Precautions should be taken when making tank breaks and flame cutters should be placed on such tanks.

2.3.26. Flammable solids

A flammable solid is a solid that can easily burn or rub, which can cause or contribute to fire.

Easily combustible solids are harmful substances or mixtures in powder, granular or paste form which readily flammable and flammable when exposed to a combustion source such as a burning match for a short period of time.

2.3.26.1. Storage

- Flammable materials should be stored in cool enough places to avoid accidental formation of airborne vapors.
- Very readily flammable substances must be separated from strong oxidizers and spontaneously flammable substances.
- The walls, ceilings and floors of the storage rooms must be made of materials resistant to fire for at least two hours.
- Storage rooms should be fitted with automatic closing fire doors.
- Electrical installations of the storage rooms should be grounded and periodically checked or automatic smoke or fire detectors should be installed in the storage rooms [25].

2.3.27. Substances and mixtures that come into the reaction spontaneously

Spontaneously reacting substances or mixtures are thermally unstable liquids or solids or mixtures which may undergo a strong exothermic decomposition even without oxygen (air) entrainment. This definition does not cover substances and mixtures classified as explosives, organic peroxides or oxidants according to this division.

2.3.27.1. Storage

- The self-accelerating decomposition temperature (SADT) of spontaneously reacting substances is the lowest temperature at which SADT enters self-accelerating decomposition. A fire or explosion may result from this reaction. The chemically reacted chemicals must be 10-20^{o}C below their ADT.
- It is also dangerous to store certain substances that enter the spontaneous reaction under a certain temperature. Some dissolved in the solvent crystallize below certain temperatures, which makes them more sensitive. Self-reactive substances dissolved in water should not be stored below 0^{o}C.
- It should be kept away from sunlight and heat sources.
- It must be protected from bumps and shakes.
- Containment must be protected.
- It should be stored in dry and well ventilated place.
- It must be stored in tightly closed containers.
- It should be stored away from other materials.

2.3.28. Pyrophoric liquids

Pyrophoric liquid is a liquid substance or mixture that can spontaneously ignite within five minutes after entering the air with the air, even in very small quantities.

Where the pyrophoric liquid is placed in an inert carrier, it ignites within 5 minutes in contact with air, or it ignites a filter paper within 5 minutes.

2.3.28.1. Storage

- Pyrophoric chemicals should be stored under inert atmosphere or, if appropriate, under kerosene.
- In storage areas heat, fire, oxidizing substances and water sources should be avoided.
- Containers carrying Priforic chemicals should be labeled with appropriate labels to indicate the name of the chemical and danger warnings.
- Even small amounts of impurities can cause fire or explosion. For this reason, after use chemicals should not be put back into the container.

2.3.29. Pyrophoric solid matter

The pyrophoric solid is a solid or mixture that can be retained within 5 minutes after entering the air with the air, even in very small quantities.

Pyrophoric ignites in 5 minutes when it comes into contact with air.

2.3.29.1. Storage

When pyrophoric solids are stored, substances written in the storage of pyrophoric fluids should be applied.

2.3.30. Self-heating heating substances and mixtures

A spontaneously heated substance or mixture is a liquid or solid substance or mixture which, apart from the pyrophoric liquid or solid, is prone to spontaneous heating without the need for energy, by reaction with air; This substance or mixture differs from pyrophoric liquid or solid substances only in large quantities (kilograms) and after a long period of time (hours or days).

The spontaneous heating of a substance or mixture is the period of time during which the stepwise reaction that the substance or mixture (air) enters with oxygen. If the rate of heat loss exceeds the rate of heat loss, the temperature of the substance or mixture increases and may cause self-ignition or burning after an induction time.

2.3.30.1. Storage

- Should be stored away light, heat sources, moisture and flammable and combustible substances
- Should avoided to store at high temperatures and appropriate risk mitigation measures should be taken.
- If the material has a high risk of reaching the ignition temperature by spontaneous heating, it should be stored in an inert atmosphere.
- An air gap should be provided between the stacks/ pallets.
- It should be stored away from other materials.

2.3.31. Substances and mixtures which, in contact with water, emit flammable gases

Substances or mixtures which emit flammable gases when in contact with water are solid or liquid substances or mixtures which are prone to suddenly become flammable by reacting with water or to release flammable gases in hazardous levels.

2.3.31.1. Storage

- Should be stored in a dry and cool area.
- Should be stored in a closed container.
- Water should be kept away from moisture and oxidants.
- Carbide stores must be dry, well ventilated and fire resistant.
- The floors of the carbide storage area must be waterproof, their walls should be resistant to pressure and the roofing should be made of lightweight material.
- Containers where carbide is stored should be sealed with waterproof, airtight lids and should contain warning statements like "the carbided will be kept dry".
- Do not use sparking tools to open the carbide containers.

2.3.32. Oxidizing liquids

The oxidizing liquid is a liquid substance or mixture which does not spontaneously burn but which generally causes oxygen to form and add to the combustion of other materials.

2.3.32.1. Storage

- It should be kept away from flammable materials and ignition sources.
- It should be stored in well-ventilated and corrosive materials in appropriate cupboards.
- It should be stored in cool place and away from sunlight.
- The oxidizing liquid reacts with almost any substance. Potential for causing explosion is very high. For this reason, it should be stored in two containers inside. For example, in the first container; Cans, barrels or bathtubs.

2.3.33. Oxidizing solids

The oxidizing solid means a solid substance or mixture which is not spontaneously flammable but which can cause or contribute to the combustion of other materials by forming oxygen.

2.3.33.1. Storage

Storage of oxidizing solids should be followed as in the case of oxidizing liquids.

2.3.34. Organic peroxides

Organic peroxides are very reactive liquid or solid organic chemicals which contain the bivalent -O-O- structure and which can be regarded as hydrogen peroxide derivatives when one or two hydrogen atoms take their place of organic radicals. Mixtures of organic peroxides containing at least one organic peroxide are considered organic peroxide. Organic peroxides are thermally unstable substances or mixtures which can undergo spontaneous accelerated exothermic decomposition. They can also carry one or more of the following features:

- Prone to explosive decomposition
- Burning quickly
- Impact or friction sensitive
- It may be dangerous in the interaction with other substances.

2.3.34.1. Storage

- Keep away from sources of heat and flame with distances at least 3 m.
- It should be stored in a dry and well-ventilated place.
- Store all packages in closed or laminated hardwood or coated metal racks, untreated or rusted.
- Containers must be stored tightly closed.
- It must be protected from sunlight.
- It should be stored away from other materials (acids, alkalis, amines, flammable materials, metals and reducing agents).
- The amount of organic peroxide present in the work area must be reduced to the minimum, and should not be kept in excess of the amount necessary for the work being done.

Exercises Questions for Chapter 2 (Classification)

1. All chemicals have:

a) UN-number

b) CAS-number

c) Hazard Identification Code

2. Hazard identification code 268 warns about:

a) Corrosive solid

b) Toxic gas

c) Toxic and corrosive gas

3.) Environmentally hazardous substance has the Hazard identification code

a) 90

b) 80

c) 99

4. This CLP-pictogram is used for a chemical that is

a) flammable

b) oxidizing

c) explosive

5. This CLP-pictogram is used for

a) grenades

b) fireworks

c) gas cylinders

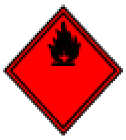
6. This CLP-pictogram warns about

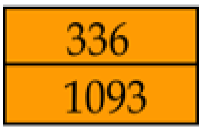
a) acute toxicity

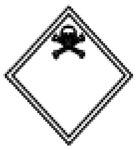
b) skin irritation

c) ccarcinogenicity

A trailer transporting chemicals have the following placards, hazard identifications code and UN-number.







7. The main hazards are

a) flammability and corrosion

b) oxidizing and toxicity

c) flammability and toxicity

8. The hazard identification code (above) has the following meaning

a) Flammable liquid, toxic, corrosive

b) Highly flammable liquid, toxic

c) Flammable liquid, toxic, which reacts with water, emitting flammable gas

9. UN-number (above) refers to the chemical of:

a) Sulphuric acid

b) Ammonia

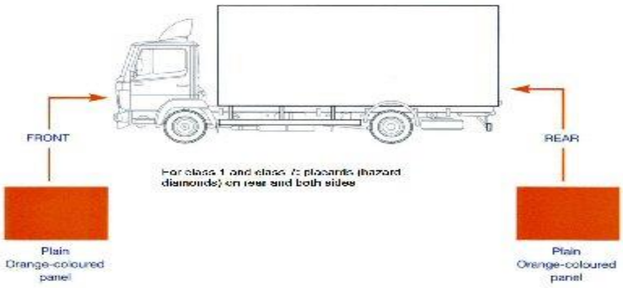
c) Acrylonitrile, stabilized

10. A plain orange plate is fixed at front and back of the "transport unit". What does that mean?

a) no hazardous materials in the "transport unit"

b) carrying packages of hazardous materials in freight containers

c) carrying empty vessels of hazardous materials



11. Hazard identification number is 20. What is the state of the substance?

a) Gas

b) Liquid

c) Solid

12. A tank has a hazard identification number of 225. What kind of material is it?

a) Refrigerated liquefied gas, oxidizing

b) Organic peroxide

c) Refrigerated liquefied gas

13. A tank has a hazard identification number of 225. What are the dangers of the material inside?

a) Toxic and causing burns

b) Causing frostbite, fire-intensifying

c) Asphyxiant

14. Hazard identification number is X462. What are the dangers?

a) Flammability and toxicity

b) Flammable solid which reacts dangerously with water, emitting flammable gas

c) Solid which reacts dangerously with water, emitting toxic gas

15. What means the following warning label?

a) Flammable solid

b) Spontaneously flammable (pyrophoric) solid

c) Oxidizing substance

16. What means the following warning label?

a) Flammable solid

b) Solid which reacts with water, emitting flammable gas

c) Explosive risk

17. What means the following warning pictogram on packages?

a) Environmentally hazardous substance

b) Oxidizing substance

c) Harmful, irritant

18. Letter combination of TFC refers to gases which are:

a) Flammable

b) Oxidative

c) Corrosive

d) Toxic

19. Warning label beside refers to hazards of

a) Flammability

b) Mass explosion

c) Toxicity

20. Warning label beside refers to

a) an autoignition hazards

b) flammable liquid

c) a flashpoint under 60 °C

21. Hazardous materials in ADR class (division) 1.5. are more dangerous than those in ADR class (division) 1.1.?

a) true

b) false

22. Non-flammable non-toxic gases are typical asphyxiant gases

a) true

b) false

23. Combustible liquids with a flash point over 93 °C are not classified as hazardous materials.

a) true

b) false

24. Hazardous materials in ADR class 4.3. cannot be spontaneously flammable.

a) true

b) false

25. Inorganic oxidative chemicals are normally combustible.

a) true

b) false

26. Toxic gases belong to ARD class 2.3.

a) true

b) false

27. Warning labels beside show a radiation level of the packages.

a) true

b) false

28. Corrosive gases belong to ARD class 2.3.

a) true

b) false

29. Substances transported at elevated temperatures typically belong to ARD class 9.

a) true

b) false

30. A hazardous material can be labelled with many different warning signs.

a) true

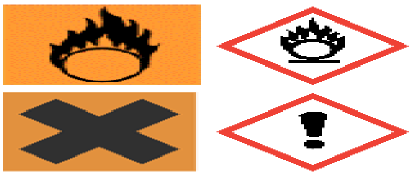
b) false

Answers for Chapter 2 (Classification)

1. B
2. C
3. A
4. B
5. C
6. A and C
7. A
8. B
9. C
10. B
11. A
12. A
13. B
14. C
15. B
16. B
17. A
18.
19.
20.
21.
22.
23.
24.
25.
26.
27.
28.
29.
30.

Exercises Questions for Chapter 2 (CLP)

1. When will the symbols with orange pictograms totally disappear from products placed on the market in the EU?



a) By June 2017

b) By the end of 2015

c) By 2020

2. Which is the given the following categories Classification of substances / mixtures according to the CLP Directive?

a) Physical Hazards, Environmental Hazards

b) Environmental Hazards, Health Hazards

c) Physical Hazards, Environmental Hazards, Health Hazards

3. On which of these products are you likely to see this symbol?

a) Fancy jewellery

b) Laundry detergent

c) Shampoo

4. Which directives have replaced the CLP Directive?

a) REACH

b) DSD

c)DSD & DPD

5. What is the label measurements of a chemical packaging with ≤ 3 litres according to the CLP directive?

a) 52x74 mm

b) 48x30 mm

c) 105x148mm

6. What does this symbol mean?

a) Possible explosion

b) Shooting target

c) Serious health hazard

7. This symbol can be found on drain cleaners. If it spills onto your eyes what should you do?

a) Rinse with water

b) Run away

c) Cool down the burning eyes

8. What is the size of the pictogram > 3 litres and ≤ 50 litres of the packaged chemical according to CLP directive?

a) 20x20 mm

b) 23x23 mm

c) 46x46 mm

9. This symbol represents various dangers to health. Which of the ones below is correct?

a) May cause an allergic skin reaction

b) Don't use when driving or operating a machine

c) No entry, private property

d) Hazardous to the aquatic environment

10. The precautions and pictograms that are being used with the CLP Directive are given below Which one is correct?

a) R  Code -

b) H  Code -

c) H  Code -

11. Which of the following is the environmental hazard classification criteria?

a) Flammable Solids

b) Acute Toxicity

c) Chronic Aquatic

12. How many classes are separated by the explosives in the classification of the substance / mixture?

a) 5

b) 6

c) 2

13. What do the P phrases in the CLP Directive mean?

a) Risk Assessment

b) Prevention Assessment

c) Hazard Pictogram

14. The damage and expression codes for health start from the following series H.

a) H300

b) H200

c) H400

15- Which of the following is not the physical hazard of the classification of the substance / mixture?

a) Explosives

b) Flammable liquids

c) Toxicity

16-According to which legislation classification of substances and mixtures is made?

a) CLP

b) REACH

c) DSD

17. The damage and expression codes for the environment start from the following series H.

a) H300

b) H200

c) H400

18. What does the CLP Directive cover?

a) Substance

b) Mixture

c) Substance and mixture

19. Which one of the following hazard statements is wrong to use?

a) Danger - Notice

b) Danger

c) Notice

20. What should you do with a product marked with this symbol?

a) Drink it

b) Do not use

c) Handle it with caution, it may be fatal

21. A mixture; is a solution composed of two or more substances.

a) true

b) false

22. A Pictogram that indicates the relative level of severity of hazards to alert the potential reader of the hazard; the following two levels are distinguished.

a) true

b) false

23. Explosive article is an article containing one or more explosive substances.

a) true

b) false

24. Classification of substances and mixtures make according to the CLP Directive.

a) true

b) false

25. $\frac{100}{\mathrm{ATE}_{\mathrm{mix}}} = \sum_{n} \frac{C_i}{\mathrm{ATE}_i}$

Acute toxicity is calculated according to the above formula.

a) true

b) false

26. An SDS consists of 12 sections.

a) true

b) false

27. Packing labelling of substances and mixtures is made according to the classification pictograms.

a) true

b) false

28. Hazard symbols are not used in the classification of substances and mixtures.

a) true

b) false

29. Classification of the substance and mixture is given in Section 2 of the SDS.

a) true

b) false

30. Oxidising gas: Any gas which may, generally by providingoxygen, cause or contribute to the combustion of other material more than air does.

a) true

b) false

Answers for Chapter 2 (CLP)

1. A
2. C
3. B
4. C
5. A
6. C
7. A
8. B
9. A and D
10. C
11. C
12. B
13. B
14. A
15. C
16. A
17. C
18. C
19. A
20. B and C
21. A
22. B
23. A
24. A
25. A
26. B
27. A
28. B
29. A
30. A

Exercises Questions for Chapter 2 (Storage of Dangerous Substances)

1. To prevent dangerous interaction, dangerous goods should be …………………… from all other goods with which they are not compatible?

a) Segregated

b) Separated

c) Alphabetically stored

2. Segregation of dangerous substances are done according to:

a) Hazard class

b) Compatibility chart

c) Amount stored

3. Acid chemicals should not be stored in metal drums

a) True

b) False

4. What is the first thing that you should do before storing a dangerous substance?

a) Check the SDS supplied from the manufacturer

b) Open the packing

c) Place it an empty space within the warehouse

5. Phenol is a ………………. chemical.

a) Toxic

b) Flammable

c) Corrosive

6. Packaging containers can be

a) Plastic

b) Metal

c) Composite (combination of metal and plastic)

7. Which of the followings are of required characteristics for packaging containers?

a) Material that is made of

b) Shape

c) Size

8. Which of the followings is not necessary for the location of a warehouse?

a) Distance from the local zone

b) Security

c) Soil structure

9. Which of them is important in warehouse buildings?

a) Enough space should be left for forklift-trucks

b) The height of the stack should not reach up to the ceiling

c) Dangerous substances should not be stored in front of fire exits

10. Which of the followings are the characteristics of the floor in the warehouse?

a) Should not be impermeable to any chemical

b) Should not be slippery

c) Should be resistant to any applied load

11. Which is wrong for out door storage of dangerous substances?

a) Asphalt should not be used as the basement material

b) Close control for any leakage is required

c) Drums can stand on the earth

12. Stands for:

a) Gases under pressure

b) Oxidising gases

c) Flammable aerosol

13. Gas cylinders should be stored away from …………

a) Smoke

b) Heat

c) Corrosive substances

14. Which of the followings statements is false?

a) Oxidizing gas cylinders should be kept away from flammable gas cylinders

b) Response to the gas leakage should be done by trained persons who wears breathing apparatus

c) Gas cylinders should be moved by Rolling

15.What type of gas is stored in the gas cylinder given here?

a) Corrosive and flammable

b) Toxic

c) Inert

16. What type of gas is stored in the gas cylinder given here?

a) Toxic

b) Corrosive

c) Flammable

17. Which of the followings is given wrong?

a) Strong oxidising agents should not be stored next to flammable liquids.

b) Cylinders containing different kind of gas must be kept together.

c) Flammable substances must be separated from strong oxidizers.

18. Which of the followings is wrong related to the handling of gas cylinders?

a) Wear always PPE such as th gloves, protective footwear, eye protection

b) Manually moving cylinders can be done by trained person for longer distances

c) It is not recommended to move the cylinder with valve and pressure regulator attached or with the valve open

19. In the storage area oxygen cylinders must be stored at least …........ away/separated by a fire wall from fuel gases such as acetylene, propane, methane etc.

a) 3 meters

b) 2 meters

c) 1 meters

20. Open head plastic drums are more appropriate for .... dangerous substances.

a) liquid

b) gas

c) solid

Answers for Chapter 2 (Storage of Dangeorous Substances)

1. A
2. B
3. A
4. A
5. A, B and C
6. A, B and C
7. A, B and C
8. C
9. A, B and C
10. A, B and C
11. C
12. A
13. A, B and C
14. C
15. A
16. A
17. B
18. B
19. A
20. C

CHAPTER 3

3. PREVENTION AND PRECUTIONS

3.1. Objectives

Prevention of chemical accidents, i.e., avoiding incidents and lessening impacts of any incidents, as well as learning from experience to control hazards and reduce risks; and preparedness for chemical accidents, i.e., being ready for accidents, and trained to act, prior to the onset of an incident. This involves putting into place the systems and resources needed for appropriate emergency response in the event of an accident.

3.2. Introduction

The process of transforming matter can be natural or artificial and chemistry has enabled man to satisfy his basic needs and constantly improve his living conditions. Chemical substances can however also be dangerous to man and his environment. Depending on the quantities involved, their degree of toxicity, corrosive power, explosive force, in flammability or even radioactivity, they can cause considerable damage. It is therefore important to know the risks linked to chemical substances, to keep to the prescribed directives for handling them and to establish prevention, protection and intervention measures in order to prevent these risks from developing.

The chemical substances used in the home and workshop are not generally dangerous, as long as the instructions for their use and storage, which usually come with the original container, are followed.

It is especially important to keep these products out of reach of children and not to transfer them to containers used for storing food.

Large quantities of these dangerous substances are produced and used in industrial and commercial enterprises. Their careless handling, transport and storage entail serious dangers for man and the environment. It is important to guard against these risks by taking the necessary preventive, precaution and protective measures. To these peace time risks are added the menace of chemical and biological weapons in times of war or crisis (terrorism), despite international laws restricting or forbidding their use. Protective measures against these are generally designed and taught by the military within the framework of civil protection.

The prevention of accidents involving hazardous substances is the concern of all stakeholders including: industry (e.g., owners and managers of hazardous installations, other employees and (sub) contractors working at or on behalf of such installations, and employee representatives); public authorities at national, regional and local levels; and communities.

- For accident prevention activities to be effective, co-operative efforts should be undertaken among relevant parties, at all levels. Within communities where there are hazardous installations, it is important for industry, local authorities and the public to work together to reduce risks of accidents.
- This co-operation should be based on a policy of openness which will, among other things, help increase public confidence that appropriate measures are being taken to limit the risk that accidents involving hazardous substances will have off-site effects.

3.3. Prevention

The chemical industry has been at the forefront of disaster prevention. Industrial disasters on the scale of Seveso and Bhopal prompted chemical firms to rethink their response to accidents, and, more generally, how they do business.

Chemical companies are working to prevent chemical accidents and reduce their impact. Global and regional networks are a crucial part of this strategy. In Europe the International Chemical Environment (ICE) network of emergency professionals provides information, practical help and equipment to the competent emergency authorities to cope with chemical incidents.

Preventing chemical accidents is simple. Follow the instructions regarding the chemical whether in industry or at home. Should a chemical risk occur outside your home, your local Emergency Alert System or EAS will keep you informed by television or radio. Following directions is the surest way to keep you and your family safe from chemical spills and other accidents.

Types of alerts that may present themselves are pesticide exposure, power outages, toxic releases from tanker accidents or factories, and terror attacks.

In most cases you will be able to manage your chemical safety in-house. You will be familiar with the types of chemicals involved and the type of work activities in which these chemicals are used. In addition, your employees will have experience and knowledge that you can use when deciding on the precautions you are going to take.

You will probably already have precautions in place. You are now checking if these are sufficient and if you need to take further steps to protect people. Small or low-risk businesses will find it straight forward to identify their chemical hazards and put in place appropriate control measures. Larger businesses, and particularly those working in high-risk sectors, may need more resources and competency to manage their chemical safety.

Prevention of injuries, accidents and incidents in the chemical industry in the European Union and Turkey. Approaches to prevention of accidents, incidents and accidents in the EU and Turkey are similar, but have their own characteristics.

Table.3.1. Prevention of injuries, accidents and incidents in the chemical industry in the EU.

Responsible Authorities Ministry of the Environment; Ministry of the interior; Mining Offices; Environmental Inspectorates; Regional offices; State Labour Inspection Offices; Administrative offices for fire protection civil protection and the integrated rescue system; Regional health offices; Integrated control of major accident prevention.	**Methods and Means** Analysis and Risk Assessment; Safety program for prevention of major accidents; Safety Report; Training of personnel; Control over compliance with requirements for safety; The plan of physical protection of the building or equipment; Emergency plans.
State Control Territorial management of the building permit; EIA (Environmental Impact Assessment of environment); Process of IPPC (integrated authorization	**Informing the Public** Information to the public for discussion and approval of safety documentation; Information to the public about major accident hazards, the preventive measures and behaviour of citizens in the event of a

operation); Building permits; Approval of safety documentation; Registration of hazardous production facilities in the state register; Assessment of safety; Liability insurance for damage caused by major accidents; Technical investigations into the causes of accidents; Regular inspection of dangerous object.	serious accident; Information to the public during an accident.

3.3.1. Methods and means of prevention of injuries, incidents and accidents in the European Union

Analysis and evaluation of risks, which mainly contains the following parts:

(a) Identification of sources of risk (hazard);

(b) Identification of accident scenarios of events and their causes;

(c) Estimation of the impact of accident scenarios on the health and lives of people, livestock, environment and property;

(d) Estimation of likely accident scenarios;

(e) Determination of the level of risk;

(f) Evaluation of the acceptability of the risk of serious accidents.

Plan of physical protection of industrial object, which focuses on the following aspects:

(a) Analysis of the possibility of unauthorized activity or a possible attack on buildings or equipment;

(b) Regime measure;

(c) Physical safety;

(d) Safety of technical means.

Safety Program (or a safety report) to prevent serious accidents, which mainly contain the following parts:

(a) Principles of prevention of major accidents;

(b) Composition of safety management system to ensure the health and lives of people, livestock, environment and property;

(c) Determination of principles of safety and reliability according to risks identified during construction, operation and maintenance of any facilities, equipment and infrastructure connected with its operation, which represent a major accident hazard (only applies to a safety report);

(d) Development of principles of the internal emergency plan and provision of information to create external emergency plans in order to take necessary measures in case of a serious accident (applies only to the safety report);

(e) Provision of appropriate information to the competent public authorities and municipalities to reach a decision in terms of new activities or developments around existing buildings or facilities (only applies to a safety report).

Table.3.2. Features and characteristics of a management system for process safety.

Planning Explicit goals and objectives Well-defined scope Clear-cut desired outputs Consideration of alternative achievement mechanisms Well-defined inputs and resource requirements Identification of needed tools and training	**Organizing** Strong sponsorship Clear lines of authority Explicit assignments of roles and responsibilities Formal procedures Internal coordination and communication
Implementing Detailed work plans Specific milestones for accomplishments Initiating mechanisms	**Controlling** Performance standards and measurement methods Checks and balances

	Performance measurement and reporting Internal reviews Variance procedures Audit mechanisms Corrective action mechanisms Procedure renewal and reauthorization

3.4. Roles of stakeholders

One important aspect of any effective programme for chemical accident prevention and preparedness is the involvement of all the relevant stakeholders. Generally, industry has primary responsibility for the safety of their hazardous installations. Government authorities are responsible for setting policies and objectives, establishing and implementing laws and programmes to help protect human health, the environment, and property, and motivating all stakeholders to act safely. Other stakeholders also have roles to play and, in particular, the communities where the installations are located.

The following is a summary of “best practices” related to the roles and responsibilities of the different stakeholders (*i.e.*, goals to be achieved over time) from the OECD *Guiding Principles on Chemical Accident Prevention, Preparedness and Response* (2nd ed., 2003).

3.4.1. Role of all stakeholders

- Make chemical risk reduction and accident prevention, as well as effective emergency preparedness and response, priorities in order to protect health, the environment, and property.
- Communicate and cooperate with other stakeholders on all aspects of accident prevention, preparedness, and response.

3.4.2. Role of industry (including management and workers)

3.4.2.1. Management

- Know the hazards and risks at installations where there are hazardous substances.
- Promote a “safety culture” that is known and accepted throughout the enterprise.

- Establish safety management systems and monitor/review their implementation.
- Utilise “inherently safer technology” principles in designing and operating hazardous installations.
- Be especially diligent in managing change.
- Prepare for any accidents that might occur.
- Assist others to carry out their respective roles and responsibilities.
- Seek continuous improvement.

3.4.2.2. Workers

- Act in accordance with the enterprise’s safety culture, safety procedures, and training.
- Make every effort to be informed and to provide information and feedback to management.
- Be proactive in helping to inform and educate your community.

3.4.2.3. Role of government authorities

- Seek to develop, enforce, and continuously improve regulations, policies, and practices.
- Provide leadership to motivate all stakeholders to fulfil their roles and responsibilities.
- Monitor the industry to help ensure that risks are properly addressed.
- Help ensure that there is effective communication and cooperation among stakeholders.
- Promote inter-agency coordination.
- Know the risks within your sphere of responsibility and plan appropriately.
- Mitigate the effects of accidents through appropriate response measures.
- Establish appropriate and coherent land-use planning policies and arrangements.

3.4.4.4. Role of other stakeholders (*e.g.,* communities/public)

- Be aware of the risks in your community and know what to do in the event of an accident.
- Participate in decision-making relating to hazardous installations.
- Cooperate with local authorities and industry in emergency planning and response.

3.4.5. Components of a major hazard control system

3.4.5.1. Definition and identification of major hazard installations

Competent authorities should make arrangements for both existing and proposed new major hazard installations to be clearly defined and identified by a list of hazardous substances or categories of substances and associated threshold quantities, which should include:

(a) very toxic chemicals such as:

- methyl isocyanate;
- phosgene;

(b) toxic chemicals such as:

- acrylonitrile;
- ammonia;
- chlorine;
- sulphur dioxide;
- hydrogen sulphide;
- hydrogen cyanide;
- carbon disulphide;
- hydrogen fluoride;
- hydrogen chloride;
- sulphur trioxide;

(c) flammable gases and liquids;

(d) explosive substances such as:

- ammonium nitrate;
- nitro glycerine;
- trinitrotoluene.

The definition and identification of major hazard installations by the competent authorities should be arranged in such a way that they allow priorities to be set for those installations requiring particular attention.

3.4.5.2. Information about the installations

The works managements of all major hazard installations should notify details of their activities to the competent authorities.

For major hazard installations within the scope of the definition, a safety report should be prepared by the works management. This should include:

(a) technical information about the design and operation of the installation;

(b) details on the management of its safety;

(c) information about the hazards of the installation, systematically identified and documented by means of safety studies;

(d) information about the safety precautions taken to prevent major accidents and the emergency provisions that should reduce the effects of such accidents.

This information should be made available by the works management to all parties concerned in major hazard control systems, including workers, workers' representatives, competent authorities and local authorities where appropriate. These parties should respect the confidentiality of information obtained in the conduct of their duties, in accordance with national law and practice.

For the competent authorities the information should:

(a) give insight into the plant and its hazards;

(b) allow the evaluation of these hazards;

(c) allow licence or permit conditions to be determined where appropriate;

(d) allow priorities to be set for the inspection of major hazard installations in their country or state;

(e) allow the preparation of off-site emergency plans (where appropriate).

The information should be systematically arranged in such a way that parts of the installation which are critical to its safety are clearly identified, possibly by the use of rapid ranking systems.

3.4.5.3. Assessment of major hazards

Major hazard installations should be assessed by works management and, depending on local arrangements, by the competent authorities.

This assessment should identify uncontrolled events which could lead to a fire, an explosion or release of a toxic substance. This should be achieved in a systematic way, for example by means of a hazard and operability study or by checklists, and should include normal operation, start-up and shut-down.

The consequences of a potential explosion, fire or toxic release should be assessed using appropriate techniques and data. These will include:

(a) estimation of blast waves, overpressure and missile effects in the case of an explosion;

(b) estimation of thermal radiation in the case of a fire;

(c) estimation of concentration profiles and toxic doses in the case of a toxic release.

Particular attention should be paid to the potential for domino effects from one installation to another.

The assessment should consider the suitability of the safety measures taken for the hazards identified in order to ensure that they are sufficient.

The assessment of major hazards should take account of the likelihood of a major accident taking place, although not necessarily in the form of a full quantified risk analysis.

3.4.5.4. Control of the causes of major industrial accidents

Works management should control major hazard installations by engineering and management practices, for example by:

(a) good plant design, fabrication and installation, including the use of high-standard components;

(b) regular plant maintenance;

(c) good plant operation;

(d) good management of safety on site;

(e) regular inspection of the installation, with repair and replacement of components where necessary.

Works management should consider the possible causes of major accidents, including:

(a) component failure;

(b) deviations from normal operation;

(c) human and organisational errors;

(d) accidents from neighbouring plant or activities;

(e) natural occurrences and catastrophes, and acts of mischief.

3.4.5.5. Safe operation of major hazard installations

The primary responsibility for operating and maintaining the installation safely should lie with works management.

Good operational instructions and sound procedures should be provided and enforced by works management.

Works management should ensure that workers operating the installation have been adequately trained in their duties.

Accidents and near misses should be investigated by works management.

3.4.5.6. Emergency planning

Emergency planning should be regarded by works management and the competent authorities as an essential feature of a major hazard control system.

The responsibility for on-site emergency planning should lie with Works management. Depending on local arrangements, the responsibility for off-site emergency planning should lie with local authorities and works management.

The objectives of emergency planning should be:

(a) to localise any emergencies that may arise and if possible contain them;

(b) to minimize the harmful effects of an emergency on people, property and the environment.

Separate plans should be established for possible emergencies on site and off site. These should give details of appropriate technical and organisational procedures

to reduce the effects and damage:

(a) to people, property and the environment;

(b) both inside and outside the installation.

The emergency plans should be clear and well defined, and available for use quickly and effectively in the event of a major accident. On-site and off-site plans should be co-ordinated for maximum efficacy.

In industrial areas where available emergency equipment and manpower are limited, works management should attempt to make provisions for mutual assistance between the neighbouring industrial activities in the event of a major accident.

3.4.5.7. Siting and land-use planning

Competent authorities should make reasonable attempts to ensure that there is appropriate separation between major hazard installations and:

(a) facilities such as airports and reservoirs;

(b) neighbouring major hazard installations;

(c) housing and other centres of population nearby.

3.4.5.8. Inspection of major hazard installations

Major hazard installations should be regularly inspected in order to ensure that the installations are operated according to the appropriate level of safety. This inspection should be carried out both by a safety team which includes workers and workers' representatives and separately by inspectors from competent authorities. Both types of inspection may be carried out in other ways where appropriate.

Safety personnel from the installation within this safety team should be independent of production line management and should have direct access to works management.

Inspectors from competent authorities should have the legal right to free access to all information available within the installation that is necessary in pursuit of their duties, and to consultation with workers' representatives.

3.5. Duties of competent authorities

Competent authorities should define appropriate safety objectives, together with a major hazard control system for their implementation.

Although the control of major hazards is primarily the responsibility of the works management operating a major hazard installation, this major hazard control system should be set up by the competent authorities in consultation with all interested parties.

Such a system should include:

(a) the establishment of an infrastructure;

(b) the identification and inventory of major hazard installations;

(c) receipt and evaluation of safety reports;

(d) emergency planning and information to the public;

(e) siting and land-use planning;

(f) inspection of installations;

(g) reporting of major accidents;

(h) investigation of major accidents and their short- and long-term effects.

3.5.1. Establishment of infrastructure for a major hazard control system

Competent authorities should establish contacts with the industry at various levels. Such contacts should allow discussion and co-ordination of the various administrative and technical issues concerning major hazard installations and their control.

Competent authorities should make available sufficient expertise to carry out their responsibilities within the major hazard control system.

Where the expertise for a particular aspect of major hazard control is not available within the competent authorities, they should arrange for that expertise to be made available from outside, for example from industry or from external consultants.

Those who provided expertise at the request of the competent authorities should not disclose the information which they have learned in connection with their service to any outside body other than the competent authorities.

3.5.2. Establishment of an inventory of major hazard installations

The implementation of a major hazard control system should start with the identification of major hazard installations. The competent authorities should draw up a definition of major hazard installations using criteria selected for their country or state.

These criteria should be established to take account of national priorities and available resources.

Legislation should be established by competent authorities requiring works managements to notify them where their works fall within the scope of the definition of a major hazard installation.

The notification should include a list of hazardous substances and quantities present which qualify the installation to be classified as a major hazard installation.

3.5.3. Receipt and evaluation of safety reports

A deadline should be set by the competent authorities for a safety report to be submitted or made available to them by the works management, and for its subsequent updating.

The competent authorities should make arrangements so that they may adequately evaluate these safety reports. This evaluation should include:

(a) examination of the information, to check for completeness of the report;

(b) appraisal of the safety of the installation;

(c) on-site inspection to verify some of the information given, preferably on selected safety-relevant items.

The evaluation should preferably be carried out by a team of specialists, covering the various disciplines involved, where necessary with the help of external independent consultants.

3.5.4. Emergency planning and information to the public

Competent authorities should establish arrangements for an on-site emergency plan to be drawn up by the works managements of each major hazard installation.

Competent authorities should establish arrangements for an off-site emergency plan to be drawn up by local authorities and works management, depending on local arrangements. Such a plan should be prepared in consultation with the various bodies involved: fire authorities, police, ambulance services, hospitals, water authorities, public transport, workers and workers' representatives, and so on.

These arrangements should ensure that the off site plan is consistent with the on-site emergency plan.

These arrangements should cover the need for regular rehearsals to be carried out in order to keep the off-site emergency plan in a state of readiness.

Competent authorities should make arrangements to provide safety information to the public nearby.

3.5.5. Siting and land-use planning

Competent authorities should establish a land-use policy to separate, where appropriate, major hazard installations from people living or working nearby.

Consistent with this policy, competent authorities should make arrangements to prevent encroachment of population nearer to existing major hazard installations.

For situations where existing major hazard installations are not adequately separated from populated areas, a plan for gradual improvement should be established.

3.5.6. Inspection of installations

Competent authorities should make arrangements to have major hazard installations inspected regularly.

Competent authorities should provide adequate guidance and training to enable their inspectors to carry out appropriate inspection of major hazard installations.

Inspection by competent authorities should be consistent with the risks from the major hazard installation. Based on the evaluation of the safety report of a major hazard installation, a specific inspection programme should be drawn up. The aim should be to establish a list of specific safety-relevant items in the installation, with the necessary frequency of inspection.

3.5.7. Reporting of major accidents

Competent authorities should establish a system for the reporting of major accidents by works managements.

3.5.8. Investigation of major accidents

Competent authorities should make adequate arrangements to investigate major accidents and their short- and long-term effects.

Such investigations should make use of relevant accident reports and other information available.

Competent authorities should study and evaluate major accidents occurring world-wide in order that lessons can be learnt in relation to similar installations in their countries.

3.6. Responsibilities of works management

Works management operating a major hazard installation should:

(a) provide for a very high standard of safety;

(b) organise and implement the on-site component of the major hazard control system;

(c) contribute to the drawing up and implementation of an offsite emergency plan.

3.6.1. Analysis of hazards and risks

Works management should carry out a hazard analysis of the major hazard installation.

This hazard analysis should be sufficient to enable:

(a) the safety system to be analysed for potential weaknesses;

(b) the residual risk to be identified with the safety system in place;

(c) optimum measures to be developed for technical and organisational protection in the event of abnormal plant operation.

To carry out a hazard analysis, a suitable method should be applied, such as:

- preliminary hazard analysis (PHA);
- hazard and operability study (HAZOP);
- event tree analysis;
- fault tree analysis;
- accident consequences analysis;
- failure modes and effects analysis;
- check-list analysis.

This method should be chosen according to the nature and the complexity of the major hazard installation, and should take account of the protection of workers, the public and the environment.

3.6.2. Determination of causes of major industrial accidents

An analysis of hazards should:

(a) lead to the identification of potential hardware and software failures, process and design deficiencies and human error;

(b) determine what action is necessary to counteract these failures.

In determining potential causes, the failure of hardware components should be considered.

The analysis should show whether these components can withstand all operational loads in order to contain any hazardous substance.

The component examination should indicate where additional safeguards are required and where the design should be altered or improved.

Component failures should be avoided by an in-depth examination of the operational procedures and of the behaviour of the entire installation in the case of any abnormal operation, and start-up and shut-down.

An analysis of potential accidents should include outside accidental interferences, both human and natural.

Human ability to run a major hazard installation safely should be studied in detail, not only for normal operation but also for abnormal conditions, and start-up and shut-down.

Workers operating major hazard installations should be adequately trained by works management.

3.6.3. Safe design and operation of major hazard installations

Works management should seek to ensure in the design of their installation that the quantities of hazardous substances stored and used on site are the minimum consistent with their operational needs.

Works management should ensure that all operating conditions are considered in the design of components for the major hazard installation.

Particular attention should be paid to all aspects of components containing large amounts of hazardous substances.

For the manufacture of these components, works management should pay special attention to quality assurance. This should include the selection of an experienced manufacturer, inspection and control of all stages of manufacturing, and quality control.

When assembling the installation on site, works management should pay special attention to assuring the quality of on-site work such as welding, third party inspection and functional tests before start-up of the installation.

After careful design, manufacture and assembly of a major hazard installation, works management should secure safe operation through:

(a) good operation and control procedures;

(b) sound procedures for the management of changes in technology, operations and equipment;

(c) provision of clear operating and safety instructions;

(d) routine availability of safety systems;

(e) adequate maintenance and monitoring;

(f) adequate inspection and repair;

(g) proper training of workers.

3.6.4. Measures to minimise the consequences of major accidents

Works management should plan and provide measures suitable to mitigate the consequences of potential accidents.

Mitigation should be effected by safety systems, alarm systems, emergency services, and so on.

For every major hazard installation an on-site emergency plan should be drawn up in consultation with the safety team.

Depending on local arrangements, in cooperation with the relevant local authorities, an off-site emergency plan should be developed and implemented.

3.6.5. Reporting to competent authorities

The works management of a major hazard installation should provide the competent authorities with:

(a) the notification of a major hazard installation which will identify its nature and location;

(b) a safety report containing the results of the hazard assessment;

(c) an accident report immediately after a major accident occurs.

Works management should provide these reports, and update them, as specified in local arrangements.

A safety report should document the results of a hazard analysis and inform the authorities about the standard of safety and the potential hazards of the installation.

A brief accident report containing relevant information on the nature and consequences of an accident should be delivered to the competent authorities by works management immediately after an accident occurs.

A full accident report containing information on the causes, the course and the scope of the accident, as well as lessons learnt from it, should be given to the competent authorities by works management within the specified time.

3.6.6. Information to and training of workers

In view of the crucial role of workers in the prevention of major accidents, works management should make sure that:

(a) workers have a broad understanding of the process used;

(b) workers are informed of the hazards of substances used;

(c) workers are adequately trained.

This information and training should be provided in an appropriate language and manner.

3.6.7. Duties and rights of workers

3.6.7.1. Duties of workers

Workers should carry out their work safely and not compromise theirability, or the ability of others, to do so. Workers and their representatives should cooperate with works management in promoting safety awareness and two-way communication on safety issues, as well as in the investigation of major accidents or near misses which could have led to a major accident.

Workers should be required to report forthwith to the works management any situation which they believe could present a deviation from normal operating conditions, in particular a situation which could develop into a major accident.

If workers in a major hazard installation have reasonable justification to believe that there is a serious and imminent danger to workers, the public or the environment, they should, within the scope of their job, interrupt the activity in as safe a manner as possible. As soon as possible thereafter, workers should notify works management or raise the alarm, as appropriate.

Workers should not be placed at any disadvantage because of them actions referred to above.

3.6.7.2. Rights of workers

Workers and their representatives should have the right to receive comprehensive information of relevance to the hazards and risks connected with their workplace. In particular, they should be informed of:

(a) the chemical names and composition of the hazardous substances;

(b) the hazardous properties of such substances;

(c) the hazards of the installation and precautions to be taken;

(d) full details of the emergency plan for handling a major accident on site;

(e) full details of their emergency duties in the event of a major accident.

Workers and their representatives should be consulted before decisions are taken on issues relevant to major hazards. In particular, this includes hazard and risk assessment, failure assessment and examination of major deviations from normal operating conditions.

3.6.7.3. Duties of the international supplier of technology involving major hazards

The supplier of technology and equipment should indicate to the competent authorities and works managements in the technology-receiving country whether the technology or equipment involves an installation which would be classified as a major hazard installation in the supplier's country, or elsewhere, if known.

Where technology or equipment would create a major hazard, the supplier should provide, in addition, information on the following aspects:

(a) an identification of the hazardous substances, their properties, the quantities involved and the manner in which they are stored, processed or produced;

(b) a thorough review of the technology and equipment in order to show:

- how control and containment of the hazardous substances could fail;
- how accidents could occur;
- the consequences of accidents;
- the vulnerability of the installation to abnormal external events such as power dips and failures, floods, earthquakes, unusual climatic conditions and sabotage, and their effects;
- the measures that can be taken to counteract these potential accidents;

(c) the management of the systems to prevent accidents from occurring, including:

- the use of design standards;
- the provision of protective devices;
- maintenance requirements;
- inspection and testing schedules;
- plant modification controls;
- operating procedures;
- training requirements;
- safeguards against deviations from the process.

(d) emergency planning based on the consequences of possible accidents assessed under

(e) above, including:

- procedure for raising the alarm;
- requirements and responsibilities for workers dealing with emergencies;
- necessary fire-fighting requirements and procedures;
- procedures for limiting an accident and mitigating its consequences;
- emergency medical services, procedures and supplies;
- plant shut-down procedures;
- procedures for re-entering a plant where a major accident has occurred;

(f) safety performance and accident history of similar plants elsewhere, as available.

According to contractual obligations, the supplier should provide updated safety information as it becomes available, and assistance as necessary.

3.6.8. Use of consultancy services

Works management and competent authorities should make use of consultancy services if their expertise is not adequate to cover all tasks to be fulfilled in a major hazard control system (see Annex I). On the other hand, consultancy services should not be relied upon to the exclusion of local management expertise.

Consultancy services may provide different fields of expertise, such as:

(a) hazard assessment;

(b) safe design and operation;

(c) analysis of potential accidents;

(d) establishment of on-site and off-site emergency plans;

(e) preparation of reports;

(f) training on major hazard control;

(g) assistance in the event of an emergency involving major hazards;

(h) quality assurance.

Consultants should be experienced in the relevant technology of the major hazard installation to enable them to give independent advice to organisations requiring assistance.

3.7. Prerequisites for a major hazard control system

The prerequisites for the operation of a major hazard control system are:

(a) manpower, within industry as well as within the competent authorities, including external expertise if necessary;

(b) equipment;

(c) information sources.

3.7.1. Manpower requirements

For a fully operational major hazard control system, competent authorities should ensure the availability of the following specialised manpower:

(a) government inspectors with specialist support;

(b) specialists on hazard and risk assessment;

(c) specialists on examination and testing of pressure vessels;

(d) emergency planners;

(e) experts on land-use planning;

(f) emergency services, police, fire authorities and medical services.

Competent authorities should not wait for the availability of specialised manpower in all fields before starting a major hazard control system.

3.7.2. Equipment

Competent authorities should consider whether elements of the major hazard control system require the use of computer systems, particularly in establishing data banks and national or state inventories of major hazard installations.

Depending on local arrangements, works management or local authorities should make available technical equipment, for use in an emergency situation, in accordance with the needs of the emergency plans. Such equipment should include:

(a) first-aid and rescue material;

(b) fire-fighting equipment;

(c) spill containment and control equipment;

(d) personal protective equipment for rescue personnel;

(e) measuring instruments for various toxic materials;

(f) antidotes for the treatment of people affected by toxic substances.

3.7.3. Sources of information

Competent authorities should determine their information needs for establishing a major hazard control system. These may include:

(a) technological developments in the process industries;

(b) developments in major hazard control;

(c) codes of practice of safety-related technical issues;

(d) accident reports, evaluation studies and lessons learnt;

(e) inventory of experts and specialists on major hazard control

3.8. Control of the causes of major industrial accidents

The primary responsibility for the control of the causes of major industrial accidents should lie with works management.

In determining which failure may be of importance for an individual installation, the following list of possible causes should be included:

A. Component failure

As a fundamental condition for safe operation, components should withstand all specified operating conditions in order to contain any hazardous substances in use.

An in-depth examination of the operational procedures (manual and automatic) should be carried out by works management to determine the consequences of deviations from normal operating conditions.

B. Deviations from normal operating conditions

An in-depth examination of the operational procedures (manual and automatic) should be carried out by works management to determine the consequences of deviations from normal operating conditions.

C. Human and organisational errors

As human factors in the running of major hazard installations are of fundamental importance, both for highly automated plants and for plants requiring a great deal of manual operation, human and organisational errors and their influence on safety should be examined in detail by works management in co-operation with workers and their representatives.

D. Outside accidental interferences

To ensure the safe operation of major hazard installations, potential outside accidental interferences should be carefully examined by works management including, as appropriate, accidents involving:

(a) road, rail and ship transport (especially carrying hazardous substances);

(b) loading stations for hazardous substances;

(c) air traffic;

(d) neighbouring installations, especially those handling flammable or explosive substances;

(e) mechanical impact such as that caused by a falling crane.

E. Natural forces

Depending on the local situation, the following natural forces should be considered by works management in the installation design:

(a) wind;

(b) flooding;

(c) earthquakes;

(d) settlement as the result of mining activities;

(e) extreme frost;

(f) extreme sun;

(g) lightning.

If such hazards are known to occur in the natural environment of the installation, adequate precautions should be taken against them.

F. Acts of mischief and sabotage

Every major hazard installation can be a target for mischief or sabotage. Protection from such actions, including site security, should be considered by works management in the design.

3.8.1. Rules for safe installations

The safe operation of a major hazard installation should be the responsibility of works management.

Works management should take account of all hazards identified in the hazard analysis together with possible technical and organisational control measures.

Measures used to control hazards should include:

- component design;

- manufacture of components;
- assembly of the installation;
- process control;
- safety systems;
- monitoring;
- management of change;
- inspection, maintenance and repair;
- training of workers;
- supervision;
- control of contract work.

3.8.2. Component design

Each component of a major hazard installation, such as reaction vessels, storage tanks, pumps, blowers and so on, should be designed to withstand all specified operating conditions.

Works management should ensure that the following aspects are taken into consideration when designing a safety-relevant component:

(a) static forces;

(b) dynamic forces;

(c) internal and external pressure;

(d) corrosion;

(e) stresses due to large differences in temperature;

(f) loads due to external impacts (wind, snow, earthquakes, settlement);

(g) human factors.

The above aspects should be particularly considered when designing components containing flammable, explosive or toxic gases or liquids above their boiling point.

3.8.3. Manufacture of components

Works management or the technology supplier should ensure that the manufacture of components important for the safety of the installation is carried out with appropriate quality assurance measures.

Works management or the technology supplier should arrange for inspection and control measures to be carried out, when appropriate, in the manufacturer's workshop by either qualified workers or third parties.

3.8.4. Assembly of the installation

Works management or the technology supplier shouldensure that assembly of the installation on site is carried out with appropriate quality assurance measures and arrange for all on-site work on components important for the safety of the installation to be inspected by either qualified workers or third parties;

3.8.5. Process control

To keep an installation safely within the design limits, works management should provide an appropriate control system.

3.8.6. Safety systems

All major hazard installations should be equipped by Works management with safety systems, the form and design of which will depend on the hazards present in the installation.

To prevent deviations from permissible operating conditions, works management should provide the major hazard installation, as appropriate, with:

(a) sensors and controllers to monitor temperature, pressure and flow, and to initiate actions such as emergency cooling, etc.;

(b) pressure-relief systems such as:

- safety valves; or
- bursting discs;

which where necessary should be connected to a

- blow-down system;
- scrubber;
- flare; or
- containment system;
- emergency shut-down systems

To prevent failure of safety-related components, such components should be specially equipped by works management for higher reliability, for example using "diversity" (different systems doing the same job) or "redundancy" (several identical systems performing the same task).

All safety-related utility supplies, such as electricity supply to control systems, compressed air for instruments or nitrogen supply as an inert gas, should be examined by works management to determine whether a second source, e.g. emergency generators or batteries, a buffer-storage tank or an extra set of pressure gas cylinders, is necessary in the event of a primary system failure.

To determine the existence and the cause of a malfunction and to enable the proper counteraction, works management should provide a major hazard installation with alarm systems which may be connected to sensors.

Over and above the safety systems which help to keep the installation in a safe condition, protective measures should be taken by works management to limit the consequences of an accident. Such measures may include:

(a) water-spray systems (to cool tanks or to extinguish a fire);

(b) water jets;

(c) steam-spray systems;

(d) collecting tanks and bunds;

(e) foam-generating systems;

(f) detector-activated systems.

To mitigate the consequences of an accident, an emergency plan (on-site and off-site) should be drawn up by works management and local authorities in consultation with workers and their representatives. The plan should include technical as well as organisational measures.

3.8.7. Monitoring

To ensure the safety of a major hazard installation, a monitoring schedule should be prepared by works management for the condition of all safetyrelated components and systems.

A monitoring schedule should include such tasks as:

(a) checking of safety-related operating conditions both in the control room and on site;

(b) checking of safety-related components of the installation;

(c) monitoring of safety-related utilities (electricity, steam, coolant, compressed air, etc.);

(d) monitoring corrosion of critical components.

3.8.8. Inspection, maintenance and repair

Taking into account the contributions of the workers familiar with the installation, works management should draw up a plan for the inspection, maintenance and repair of the major hazard installation.

A plan for on-site inspection should include a schedule, and the equipment and procedures to be adhered to during inspection work.

For repair work, strict procedures should be specified for carrying out any tasks involving hot work, opening of normally closed vessels or pipelines, or work which could compromise a safety system or which involves any change in design or component quality. These procedures should cover the qualifications required by personnel, quality requirements for the work to be performed and requirements for the supervision of repair work.

Requirements specified in national or internationally recognised standards or practices for inspection and repair work should be considered by works management as minimum requirements for major hazard installations.

A maintenance plan should be prepared by works management specifying the different maintenance intervals, qualifications required by personnel and the type of work to be carried out. All maintenance work and defects noted should be documented in accordance with the plan.

3.8.9. Management of change

All changes in technology, operations and equipment that would fall outside current design limits should be subject to the same review as for new installations.

Before authorising a change, works management should complete documentation of the proposed change, including:

- effects on safety;
- effects on equipment and operating procedures.

3.8.10. Training of workers

The overall safety arrangements at a major hazard installation should recognise that the human factor is critical to the safety of the installation. Therefore, works management should adequately train workers in the safe operation of the major hazard installation. For new installations, this training should take place before start-up. Necessary facilities for such training should be provided by works management.

The training should include, but should not be limited to, such topics as:

(a) broad understanding of the overall process used in the installation;

(b) the hazards of the process and the substances used, and precautions to be taken;

(c) process control and monitoring of all operating conditions, including those at start-up and shut-down;

(d) operating procedures, including those in the case of malfunctions or accidents;

(e) emergency procedure exercises;

(f) experience in similar installations elsewhere, including accidents and near misses.

Safety training for workers by works management should be a continuous process. Training sessions should be repeated at regular intervals under conditions as near to reality as possible. The effectiveness of safety training should be assessed and training programmes reviewed in co-operation with workers and their representatives.

3.8.11. Supervision

Works management should provide adequate supervision of all activities performed in a major hazard installation. Supervisors should have the necessary authority, competence and training to exercise their role properly.

3.8.12. Control of contract work

Special attention should be given to work performed by outside contractors or temporary workers. Works management should ensure that work performed by outside contractors or temporary workers meets the requirements detailed in all the provisions mentioned in this chapter, as appropriate.

3.9. Emergency planning

Internal emergency plans are to be produced in line with the requirements set out in the regulations. The information required for external emergency plans is to be provided to the competent authorities.

Upper-tier establishments must comply, in particular, with provisions concerning emergency plans, as set out in Article 12 and Annex IV of Seveso III. Operators (defined as “natural or legal persons who operate or control an establishment or installation”) must draw up an emergency plan for measures to be taken inside the establishment, and must also supply information to the competent authority so that external emergency plans can be formulated.

Emergency planning should be regarded by competent authorities, local authorities and works managements as an essential element of any major hazard control system.

Emergency plans for major hazard installations should cover the handling of emergencies both on site and off site.

Works managements should ensure that the necessary standards appropriate to the safety legislation in their country are being met. They should not regard emergency planning as a substitute for maintaining good standards inside the installation.

The objectives of emergency planning should be:

(a) to localise any emergencies that may arise and if possible eliminate them;

(b) to minimise the harmful effects of an emergency on people, property and the environment.

3.9.1. Formulation of the plan

Each major hazard installation should have an on-site emergency plan.

The on-site plan should be prepared by the works management and should be related to an estimate of the potential consequences of major accidents.

For very simple installations, the emergency plan may consist merely of putting the workers on stand-by and calling in the outside emergency services.

For complex installations, the plan should be much more substantial, taking account of each major hazard and its possible interaction with the others, and should include the following elements:

(a) assessment of the size and nature of the potential accidents and the relative likelihood of their occurrence;

(b) formulation of the plan and liaison with outside authorities, including the emergency services;

(c) procedures for raising the alarm and for communicating both within and outside the installation;

(d) appointment in particular of the site incident controller and the site main controller, and specification of their duties and responsibilities;

(e) the location and organisation of the emergency control centre;

(f) the actions of workers on site during the emergency, including evacuation procedures;

(g) the actions of workers and others off site during the emergency.

The plan should set out the way in which designated workers at the site of the accident can ask for supplementary action, both inside or outside the installation, at na appropriate time. In particular, the plan should include the provision for attempting to make safe the affected part of the installation, for example by shutting it down.

The plan should contain the full sequence of key workers to be called in from other parts of the installation or from off site.

Works management should ensure that the requirements of the plan for emergency resources, both workers and equipment, are consistent with available resources which can be quickly assembled in the event of an emergency.

Works management should consider whether sufficient resources exist at the installation to carry out the plan for the various assessed accidents in conjunction with the emergency services.

Where the plan requires the assistance of the emergency services, works management should ascertain the time taken for these services to be fully operational on site and then consider whether the workers can contain the accident during all of that period.

The plan should take account of such matters as absence of workers due to sickness and holidays, and periods of installation shut-down. It should be sufficient to apply to all foreseeable variations in manning.

3.9.2. Alarms and communication

Works management should arrange for the onset of any accident or emergency to be quickly communicated to all appropriate workers and personnel off site.

Works management should inform all workers of the procedures for raising the alarm to ensure that the earliest possible action is taken to control the situation.

Works management should consider the need for emergency alarm systems, depending on the size of the installation.

Where an alarm system is installed, there should be an adequate number of points from which the alarm can be raised.

In areas where there is a high level of noise, works management should consider the installation of visual alarms to alert workers in those areas.

Works management should make available a reliable system for informing the emergency services as soon as the alarm is raised on site. The details of the communication arrangements should be agreed between works management and the emergency services, and should also be included in the off-site emergency plan.

3.9.3. Appointment of key workers and definition of duties

As part of the emergency plan, works management should nominate a site incident controller (and a deputy if necessary) to take control of the handling of the accident.

The site incident controller should be responsible for:

(a) assessing the scale of the incident (both for internal and external emergency services);

(b) initiating the emergency procedures to secure the safety of workers and minimise damage to the installation and property;

(c) directing rescue and fire-fighting operations until (if necessary) the fire brigade arrives;

(d) arranging for a search for casualties;

(e) arranging the evacuation of non-essential workers to assembly areas;

(f) setting up a communications point with the emergency control centre;

(g) assuming the responsibilities of the site main controller until he or she arrives;

(h) providing advice and information, as requested, to the emergency services.

The site incident controller should be easily identifiable by means of distinctive clothing or headwear.

As part of the emergency plan, works management should nominate a site main controller (and a deputy if necessary) who will take overall control of the accident from the emergency control centre.

The site main controller should be responsible for:

(a) deciding whether a major emergency exists or is likely, requiring the emergency services and off-site emergency plan to be implemented;

(b) exercising direct operational control of the installation outside the affected area;

(c) continually reviewing and assessing possible developments to determine the most probable course of events;

(d) directing the shutting down of parts of the installation and their evacuation in consultation with the site incident controller and key workers;

(e) ensuring that any casualties are receiving adequate attention;

(f) liaising with chief officers of the fire and police services, local authorities and the government inspectorate;

(g) controlling traffic movement within the installation;

(h) arranging for a log of the emergency to be maintained;

(i) issuing authorised statements to the news media;

(j) controlling the rehabilitation of affected areas after the emergency.

Where the emergency plan identifies other key roles to be played by workers (e.g. first-aiders, atmospheric monitoring staff, casualty reception staff), works management should ensure that these workers are aware of the precise nature of their roles.

3.9.4. Emergency control centre

Works management should arrange for the on-site emergency plan to identify an emergency control centre from which the operations to handle the emergency are directed and co-ordinated, and should provide a suitable control centre consistent with the plan.

The control centre should be equipped to receive and transmit information and directions from and to the site incident controller and other areas of the installation, as well as outside.

Where applicable, the emergency control centre should contain, for example:

(a) an adequate number of both internal and external telephones;

(b) radio and other communication equipment;

(c) a plan of the installation showing:

- areas where there are large inventories of hazardous substances;
- sources of safety equipment;
- the fire-fighting system and additional sources of water;
- sewage and drainage systems;
- installation entrances and roadways;
- assembly points;
- the location of the installation in relation to the surrounding community;

(d) equipment for measuring and indicating wind speed and direction;

(e) personal protective and other rescue equipment;

(f) a complete list of workers;

(g) a list of key workers with addresses and telephone numbers;

(h) lists of other persons present on site, such as contractors or visitors;

(i) a list of local authorities and emergency services with addresses and telephone numbers.

Works management should arrange for the emergency control centre to be sited in an area of minimum risk.

3.9.5. Action on site

The primary purpose of the on-site emergency plan is to control and contain the accident and thereby prevent it from spreading to nearby parts of the installation, and to minimise casualties.

Works management should arrange for sufficient flexibility to be included in the emergency plan to enable appropriate action and decisions to be taken on the spot.

Works management should consider how the following aspects are covered in the emergency plan:

(a) evacuation of non-essential workers to predetermined assembly points through clearly marked escape routes;

(b) designation of someone to record all workers arriving at the assembly points so that the information can be passed to the emergency control centre;

(c) designation of someone in the emergency control centre to collate lists of workers arriving at the assembly points with those involved in the accident and then to check against the list of those thought to be on site;

(d) arranging for the lists held in the emergency control centre to be updated as necessary with details of absences due to holidays and sickness, changes in persons present on site, etc.;

(e) arranging for records of workers, including names and addresses, to be kept in the emergency control centre and to be regularly updated;

(f) arranging for the authoritative release of information during any emergency of significant length, and appointing a senior manager to be the sole source of this information;

(g) procedures for rehabilitation at the end of the emergency, including instructions for re-entering the accident area.

3.9.6. Planning shut-down procedures

Works management should ensure that emergency plans for a complex installation take account of the interrelationship of its different parts, so that ordered and phased shut-downs can take place when necessary.

3.9.7. Rehearsing emergency procedures

Once the emergency plan is finalised, works management should ensure that it is made known to all workers and to external emergency services where applicable.

Works management should arrange for the emergency plan to be regularly tested, including the following elements:

(a) communications systems which would be in operation during an accident;

(b) evacuation procedures.

3.9.8. Testing and revision

Completing a comprehensive plan for handling emergencies is a major step toward preventing disasters. However, it is difficult to predict all of the problems that may happen unless the plan is tested. Exercises and drills may be conducted to practice all or critical portions (such as evacuation) of the plan. A thorough and immediate review after each exercise, drill, or after an actual emergency will point out areas that require improvement. Knowledge of individual responsibilities can be evaluated through paper tests or interviews.

The plan should be revised when shortcomings have become known, and should be reviewed at least annually. Changes in plant infrastructure, processes, materials used, and key personnel are occasions for updating the plan.

It should be stressed that provision must be made for the training of both individuals and teams, if they are expected to perform adequately in an emergency. An annual full-scale exercise will help in maintaining a high level of proficiency.

3.10. Off-site emergency planning

The off-site emergency plan should be the responsibility of the local authority and works management, depending on local arrangements.

The plan should be based on those accidents identified by works management which could affect people and the environment outside the installation.

The plan should therefore follow logically from the assessment used as the basis for the on-site emergency plan.

It is important that the plan should have sufficient flexibility to deal with emergencies other than those specifically included in the plan.

Aspects to be included in an off-site emergency plan.

The off-site emergency plan should include the following (as appropriate):

(a) organisation – details of command structures, warning systems, implementation procedures, emergency control centres, names of the emergency co-ordinating officer, the site main controller, their deputies and other key workers;

(b) communications – identification of personnel involved, communications centre, call signs, network, lists of telephone numbers;

(c) specialised emergency equipment – details of availability and location of heavy lifting gear, bulldozers, specified fire-fighting equipment, fire boats;

specialised knowledge – details of specialist bodies, firms with specialised chemical expertise and laboratories;

(e) voluntary aid organisations – details of organisers, telephone numbers, size of resources;

(f) chemical information – details of the hazardous substances stored or processed in each major hazard installation and a summary of the risks associated with them;

(g) meteorological information – arrangements for obtaining details of weather conditions prevailing at the time of an accident, and weather forecasts;

(h) humanitarian arrangements – transport, evacuation centres, emergency feeding, treatment of the injured, first aid, ambulances, temporary mortuaries;

(i) public information – arrangements for dealing with the media and informing relatives of casualties, etc.;

(j) assessment – arrangements for collecting information on the causes of the emergency, and for reviewing the effectiveness of all aspects of the emergency plan.

3.10.1. Role of the emergency co-ordinating officer

The off-site plan should identify an emergency co-ordinating officer and a deputy, if necessary, with the necessary authority to mobilise and co-ordinate the emergency services.

The emergency co-ordinating officer should take overall command of the off-site handling of the emergency.

The emergency co-ordinating officer should liaise closely with the site main controller throughout the emergency to receive regular briefing on the development of the accident on site.

3.10.2. Role of works managements of major hazard installations

Where the responsibility for preparing the off-site emergency plan lies with works management:

(a) works management should ensure that the plan is known to all organisations and personnel with a role to play in handling the emergency;

(b) it should appoint the emergency co-ordinating officer;

(c) it should arrange for the off site plan to be rehearsed and tested in conjunction with on-site exercises and to be updated from the experience gained at these rehearsals.

Where the responsibility for preparing the off-site emergency plan lies with the local authority, works management should establish a liaison with those preparing the plan and provide information to assist them in that task.

This information should include a description of possible on-site accidents with potential for off-site harm, together with their consequences and relative likelihood.

Technical advice should be provided by works management to familiarise outside organisations which may become involved in handling the emergency.

Works management should ensure that any changes in the installation or hazardous substances on site which may affect the off-site plan are passed to those responsible for producing the off-site emergency plan.

3.10.3. Role of the local authorities

Where the duty for preparing the off-site plan lies with the local authorities, they should (as appropriate) develop any necessary administrative structures or arrangements and appoint an emergency planning officer to take charge of this task. In addition, they should appoint an emergency co-ordinating officer to take overall command of subsequent off-site emergencies.

The emergency planning officer should liaise with works management to obtain the information to provide the basis for the plan. This liaison should be maintained to keep the plan up to date. Where more than one major hazard installation is operating within any local authority, that authority should make appropriate arrangements for the co-ordination of the off-site emergency plans covering every installation, to produce where necessary an overall plan.

The emergency planning officer should ensure that all those organisations which will be involved in handling the emergency off site are familiar with their roles and are able to fulfil them.

Local authorities should attempt to enlist the help of the media in the emergency planning process.

The emergency planning officer should arrange for the off site plan to be rehearsed and tested in conjunction with on-site exercises and to be updated from the experience gained at these rehearsals.

Where a major accident could result in a major spill or environmental harm requiring attention and investigation, the emergency planning officer should identify those authorities who will carry out these tasks and inform them, as appropriate, of their role in the off-site plan.

3.10.4. Role of emergency services

The roles of the police, fire and health authorities and other emergency services should be consistent with the normal practice in each country, which may entail a redistribution of the roles listed below.

The police should take responsibility for protecting life and property, and controlling traffic movements during the emergency.

Depending on local arrangements, the police should also be responsible for tasks such as controlling bystanders, evacuating the public, identifying the dead, dealing with casualties, and informing the relatives of the dead and injured.

The control of a fire on site should normally be the responsibility of a fire-brigade officer upon arrival at the site, in co-operation with Works management.

Depending on local arrangements, the fire-brigade officer may have similar responsibilities for other major accidents such as explosions and toxic releases.

Fire authorities having major hazard installations in their area should, at an early date, familiarise themselves with the location on site of all stores of flammable materials, water and foam supply points, and fire-fighting equipment.

Health authorities, including doctors, surgeons, hospitals, poison centres and ambulances, should have a vital role to play following a major accident.

Health authority services should form an integral part of an off-site emergency plan.

Health authorities should be familiar with the short- and long-term effects on people of a major accident arising from a major hazard installation in their area.

Where hazardous substances are stored or handled at major hazard installations in their area, health authorities should be familiar with the appropriate treatment for anyone affected by these substances.

3.10.5. Role of the government safety authority or inspectorate

Depending on local arrangements, government inspectors should:

(a) check to ensure that works management has properly identified potential major accidents which could affect people and the environment outside the installation, and where appropriate has provided the information required by the local authorities;

(b) check that works management has prepared an on-site emergency plan and has provided information about the plan to the local authorities;

(c) check that the organisation responsible for producing the off-site plan has made adequate arrangements for handling emergencies of all types;

(d) check to ensure that the various elements of the emergency plan have been tested and rehearsed;

e) be clear as to their expected role during the actual emergency, including advisory and monitoring duties;

(f) in the event of an emergency, advise works management and emergency coordinating officers of the suitability of an affected area for re-entry and reuse once the emergency has ended;

(g) consider whether parts of the installation or equipment should be secured for the-spot examination and subsequent testing;

(h) interview witnesses as soon as practicable after the emergency;

(i) institute any necessary action in the light of lessons learned from a major accident, including evaluating the effectiveness of the emergency plan.

3.10.6. Rehearsals and exercises

The organisation responsible for preparing the off-site plan should appropriately test its arrangements in conjunction with on-site exercises.

In particular, it should ensure that the various communication links needed for overall co-ordination are able to operate efficiently under emergency conditions.

After each rehearsal exercise, the organisation responsible for the plan should thoroughly review the exercise to correct shortcomings or omissions in the off-site plan. The effectiveness of the plan should also be reviewed following a major accident.

3.11. Information to the public concerning major hazard installations

The ultimate critical step is to ensure that each member of the community who may be affected knows what the warnings will be and what to do during an emergency, how to get additional information and when to evacuate if necessary. Some awareness campaigns are already reasonably commonplace – making people familiar with sirens for blast warnings in the vicinity of open pit or open cast mines, for example, in coastal areas for flood warnings or in buildings and plant to alert people to equipment that is about to move or to order evacuation

Competent authorities should make arrangements to provide information to the public living or working near a major hazard installation. These arrangements should require that works management make available such information in co-operation with the local authority for all existing installations, and for new installations before they start to operate.

This information should include:

(a) the designation of the installation as a major hazard installation;

(b) a broad description in simple terms of the major hazard activities in the installation, the hazardous substances used and how they are controlled;

(c) ways of recognising that an emergency is occurring (alarm system);

(d) the action that the public should take in the event of an emergency;

(e) the known effects to the public of a major accident;

(f) remedial treatment appropriate for anyone affected by a major accident.

Advice on the distance from the major hazard installation within which the public are to be informed should be obtained from the Group of Experts or elsewhere.

All different available forms of communicating this information should be considered in order to make these procedures as effective as possible, taking into account the different target groups (schools, hospitals, etc.).

The general information should periodically be repeated and if necessary updated to allow for any movement of the population into and out of the locality.

Local authorities in co-operation with works managements should assess whether the general information has been effectively communicated and understood, and take appropriate action to revise it if necessary.

Arrangements for informing the public should allow for the existence of major hazard installations operating near a territory that comes under a diferente local authority or country from the one in which the installation is situated.

Provision should be made for people living near the installation but in the adjoining territory to be similarly informed.

Prepare a standard emergency response brochure for distribution to all residents in areas that may be affected. This must be appropriate to the level of literacy of the local population – use of symbols and pictures may simplify the response actions, although this may need to be backed up by a face-to-face community education programme. The brochure may need to be in two or more languages for some communities.

3.12. Local incident surveillance and environmental monitoring

For each site identified, the chemicals present (current and planned) are identified and scenarios of possible releases are developed for each one. For each site and substance, the exposure pathways and vulnerable zone (the area to which the contaminants might be transported through air or water) are estimated and mapped out. This can often be done using computer models. It requires a thorough knowledge of the topography of the area, the waterways, the reservoirs and the prevailing climate.

The populations that could be affected within the vulnerable zone are then identified, with an emphasis on any particularly vulnerable groups (children in schools, the elderly in residential facilities, hospital patients, etc.). In addition to the residents of the vulnerable zone, other people in the area at certain times could also be affected, such as workers (both inside the plant and in its vicinity), motorists and visitors to entertainment facilities. Factors that affect vulnerability include the amount and quality of shelter, the access into and out of the site, and people's awareness of risks and response measures.

Facilities and structures in and around the vulnerable zone that provide essential services (e.g. hospitals) and which could be disabled by an incident should be identified.

Areas where contamination would have significant effects, such as farmland, water bodies used for leisure activities or wildlife support, and ecologically important sites should be considered.

3.13. Health assessment

To measure the impact of a chemical release on health, it is necessary to know the background levels of illness in the community before the release.

In most countries, health data are only available at population levels greater than that likely to be affected by a chemical incident. This can make it more difficult to identify any changes in the health of the affected population. To overcome this difficulty, routine data should be collected from populations around the chemical sites. This can be expensive, but should be considered for very high-risk sites. If routine data are not available to produce a baseline measure, a one-off survey may be considered.

In addition, it is helpful to take baseline measurements of chemical biomarkers from the people most likely to respond first to an incident, because they have a long-term risk of exposure. Ideally, these measures should be conducted by the occupational health services. The samples may be frozen and analysed after an incident, together with a post incident sample, to measure the influence of the chemical incident.

3.14. Environmental assessment

Environmental assessment, to predict the levels of environmental contamination from a variety of likely release scenarios.

3.15. Reducing the health risks of incidents

Common measures to reduce the health risks of chemical incidents include:

- locating chemical sites away from centres of population;
- registering all chemicals in commercial establishments with a hazard inventory to ensure rapid identification of the released chemical;
- regularly evaluating plans and their implementation;
- storing reduced amounts of chemicals;
- clearly labelling all chemicals in transit;
- rapidly notifying the chemical incident emergency services in the event of a chemical release;
- regularly surveying and standardizing the reporting of incidents, including small “routine” ones;
- decontaminating land or water already contaminated by waste disposal;
- preventing or containing water run-off from fire-fighting;
- constructing drainage ditches or holding tanks to contain leaked liquid chemicals.

3.16. Pros. and Cons.

There are many examples of chemical accidents – unintended spills, releases, fires, explosions – that have resulted in serious injuries, environmental catastrophes, economic hardship, and other significant harm. While some of these are well-known and even identified internationally by just a place-name (Bhopal, Seveso, Baia Mare), there have been many more that are not widely publicised. Furthermore, significant accidents continue to occur throughout the world in large and small countries and in large and small facilities.

Chemical accidents can have devastating impacts on human health and the environment. For example, they can cause direct, immediate harm to workers and others in the vicinity who are exposed to the harmful chemicals, or who are injured by an explosion or fire. Acute exposures to chemicals can also cause longer-term health consequences including chronic diseases and cancer. People can also suffer harm from indirect contact through their diet as the result of contaminated drinking water, agricultural products, fish, livestock, and other food items because of polluted air, surface water, and soil.

The release of hazardous substances into air, water, and soil can have serious environmental consequences, killing animals and vegetation, poisoning water supplies used for drinking, fishing, and irrigation, and rendering soil unfit for agriculture.

It is difficult to calculate the costs and benefits of implementing a chemical accidents programme. However, there is convincing evidence that accident prevention and preparedness is a wise investment, with the costs involved in improving safety being less than the cost of accidents. In addition to the potential impact on human health, accidents can cause significant economic harm, both to theenterprise as well as to the community. The costs associated with response, clean-up and recovery, including health response such as medical treatment, can be quite significant.

It may be obvious that the enterprise where the accident occurred may suffer significant economic losses (from, *e.g.*, property damage, loss of jobs, having to stop operations for an extended period, or even bankruptcy). What is not as obvious are the costs to other industries in the vicinity of the accident. For example, an accident may pollute local waterways increasing the costs of water used for drinking and agriculture and causing significant damage to the fishing industry. In addition, suppliers and customers of the enterprise will be impacted.

Chemical accident programmes provide indirect financial benefits, in addition to the direct savings from accident avoidance. For example, such programmes often lead to improved efficiency and lower production costs, as well as to improvements in the general health, safety, and environmental performance of enterprises.

Safe operations also protect the good will and reputation of industry and public authorities, as well as foster improved relationships with members of the local communities.

Exercises Questions for Chapter 3 (Prevention and Precautions)

1. Identification of accident scenarios and their causes is not important for the prevention of chemical accidents.

a) True

b) False

2. Is important Inform the general public on prevention of injuries, accidents and incidents in the chemical industry.

a) Information to the public for discussion and approval of safety documentation.

b) Information to the public about major accident hazards, the preventive measures and behaviour of citizens in the event of a serious accident.

c) Information to the public during an accident.

d) All previous

3. Features and characteristics of a management system for process safety

a) Planning, organizing, implementing and controlling.

b) Planning and controlling.

c) Planning, implementing and controlling.

d) Planning and implementing.

4. For major hazard installations should be prepared a safety report should include:

a) information about the safety precautions taken to prevent major accidents and the emergency provisions that should reduce the effects of such accidents.

b) technical information about the design and operation of the installation and details on the management of its safety.

c) information about the hazards of the installation, systematically identified and documented by means of safety studies.

d) all previous

5. Works management should control major hazard installations by engineering and management practices, for example by:

a) casual maintenance of the installations.

b) regular inspection of the installation, with repair and replacement of components where necessary.

c) poor plant operation.

d) weak on-site security management.

6. The objectives of emergency planning should be:

a) to minimize the harmful effects of an emergency on people, property and the environment.

b) localise any emergencies that may arise and if possible contain them.

c) only classification of risks.

d) Only the identification of the resources and resources that can be mobilized in a major accident.

7. Major hazard installations should be regularly inspected in order to ensure that the installations are operated according to the appropriate level of safety. This inspection should be carried out both by a safety team which includes workers and workers' representatives and separately by inspectors from competent authorities.

a) True

b) False

8. Duties of competent authorities in major hazard control system:

a) inspection of installations;

reporting of major accidents;

investigation of major accidents and their short- and long-term effects.

b) the identification and inventory of major hazard installations;

emergency planning and information to the public;

inspection of installations;

c) the establishment of an infrastructure;

the identification and inventory of major hazard installations;

receipt and evaluation of safety reports;

emergency planning and information to the public;

siting and land-use planning;

inspection of installations;

reporting of major accidents;

investigation of major accidents and their short- and long-term effects.

d) emergency planning and information to the public;

siting and land-use planning;

inspection of installations;

9. The works management of a major hazard installation should provide the competent authorities with:

a) the notification of a major hazard installation which will identify its nature and location.

b) a safety report containing the results of the hazard assessment and an accident report immediately after a major accident occurs.

c) the notification of a major hazard installation which will identify its nature and location.

d) accident report immediately after a major accident occurs

10. In view of the crucial role of workers in the prevention of major accidents, works management should make sure that:

a) workers are informed of the hazards of substances used and adequately trained

b) training and information actions are not relevant to accident prevention

c) this information and training should be provided in a technical language

d) workers haven´t a broad understanding of the process used

11. Workers and their representatives should be consulted before decisions are taken on issues relevant to major hazards. In particular, this includes hazard and risk assessment, failure assessment and examination of major deviations from normal operating conditions.

a) True

b) False

12. For a fully operational major hazard control system, competent authorities should ensure:

a) emergency services

b) fire authorities and medical services

c) government inspectors with specialist support

d) government inspectors with specialist support

specialists on hazard and risk assessment, specialists on examination and testing of pressure vessels, emergency planners, experts on land-use planning, emergency services, police, fire authorities and medical services.

13. The control of the causes of major industrial accidents should include possible causes:

a) human and organisational errors, component failure and deviations from normal operating conditions

b) outside accidental interferences, natural forces and acts of mischief and sabotage

c) none of the previous

d) all previous

14. The measures used to control hazards should include:

a) only safety systems

b) only training of workers

c) inspection, maintenance and repair

d) safety systems, Inspection, maintenance and repair, training of workers and monitoring

15. Which are safety systems help to keep the installation in a safe condition:

a) collecting tanks and bunds;

b) detector-activated systems

c) water-spray systems (to cool tanks or to extinguish a fire)

d) foam-generating systems;

16. To mitigate the consequences of an accident, an emergency plan (on site and off site) should be drawn up by works management and local authorities in consultation with workers and their representatives. The plan should include technical as well as organizational measures.

a) Inspection, Maintenance and Repair

b) Training of workers

c) Monitoring, Inspection, maintenance and repair and Training of workers

d) Monitoring

17. The overall safety arrangements at a major hazard installation should recognize that the human factor is critical to the safety of the installation. Therefore, works should adequately train workers in the safe operation of the major hazard installation.

a) True

b) False

18. The objectives of emergency planning should be:

a) Just localize any emergencies that may arise and if possible eliminate them

b) Just minimize the harmful effects of an emergency on people, property and the environment.

c) localize any emergencies and if possible eliminate them and minimize the harmful effects of an emergency on people, property and the environment.

d) None of the previous

19. Each major hazard installation should have an on-site emergency plan.

a) True

b) False

20. The emergency plan identifies other key roles to be played by workers (e.g. first-aiders, firefighting, atmospheric monitoring staff, casualty reception staff), works management should ensure that these workers are aware of the precise nature of their roles.

a) Training and practical exercises should be given

b) It is not necessary to inform workers about their duties in case of an accident / incident

c) Just inform the workers about their duties in case of an accident / incident

d) Training should be given to workers

21. The emergency plan should be revised when shortcomings have become known, and should be reviewed at least annually. An annual full-scale exercise will help in maintaining a high level of proficiency.

a) True

b) False

22. The off-site emergency plan should be the responsibility of: arrangements.

a) workers

b) the local authority and work management

c) work management

d) the local authority

23. The firefighters, police and health authorities and other emergency services should be familiar with the internal and external emergency plans.

a) True

b) False

24. The populations that could be affected within the vulnerable zone are

a) Just workers

b) motorists and visitors

c) residents of the vulnerable zone

d) All previous

25. The communities that may be affected with a possible accident should know what the warnings will be and what to do during an emergency, how to obtain additional information, and when to evacuate if necessary.

a) True

b) False

26. The measures to reduce the health risks of chemical incidents include:

a) location of chemical industry near population centres

b) storage of large quantities of chemicals

c) constructing drainage ditches or holding tanks to contain leaked liquid chemicals

d) rarely assess emergency plans and their implementation

27. Chemical accidents can have devastating impacts only human health.

a) True

b) False

28. There is convincing evidence that accident prevention and preparedness is a wise investment, with the costs involved in improving safety being less than the cost of accidents. In addition to the potential impact on human health, accidents can cause significant economic harm, both to the enterprise as well as to the community. The costs associated with response, clean-up and recovery, including health response such as medical treatment, can be quite significant.

a) True

b) False

29. Safe operations also protect the good will and reputation of industry:

a) just industry

b) industry and public authorities

c) industry and public authorities, as well as foster improved relationships with members of the local communities

d) just public authorities

30. Please indicate which are the principles of prevention:

a) Eliminate the hazard / evaluate the risk/ Inform and train

b) Combat risks at origin / Adapting the work to people /Attend the technical evolution

c) Substitution the dangerous by the non-dangerous or less dangerous /Plan prevention / Prioritize collective protection rather than individual protection

d) All previous

Answers for Chapter 3 (Prevention and Precautions)

1. False
2. D
3. A
4. D
5. B
6. A and B
7. True
8. C
9. C
10. A
11. True
12. D
13. D
14. D
15. B
16. C
17. True
18. C
19. True
20. A
21. True
22. B
23. True
24. D
25. True
26. C
27. False
28. True
29. C
30. D

CHAPTER 4

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4. HEALTH AND ENVIRONMENT

By their nature, the manufacture, storage, and transport of chemicals are accidents waiting to happen. Chemicals can be corrosive, toxic, and they may react, often explosively. The impacts of chemical accidents can be deadly, for both human beings and the environment.

Many if not most products we use in everyday life are made from chemicals and thousands of chemicals are used by manufacturing industries to make these products. The source of many of these chemicals is petroleum, which is refined into two main fractions: fuels and the chemical feed stocks that are the building blocks of plastics, paints, dyes, inks, polyester, and many of the products we buy and use every day. Fuels and chemical feed stocks made from petroleum are called organic chemicals. The other important class of chemicals is inorganics, which include acids, caustics, cyanide, and metals. Commercial products made from inorganics range from car bodies to computer circuit boards.

Of the more than forty thousand chemicals in commercial use, most are subject to accidental spills or releases. Chemical spills and accidents range from small to large and can occur anywhere chemicals are found, from oil drilling rigs to factories, tanker trucks to fifty-five-gallon drums and all the way to the local dry cleaner or your garden tool shed.

4.1. Where and in what form are chemicals found?

Chemicals are present in every workplace. Even in the cleanest, most modern office, employees may be routinely exposed to inks, toners and adhesives not to mention a wide range of chemicals used in cleaning and maintenance.

4.1.1. Chemicals can exist in many forms

- Dust, fumes, fibres, powders.
- Liquids.
- Gases, vapours, mists.

Any chemical, in either gas, liquid or solid form, that has the potential to cause harm is referred to as a hazardous or dangerous chemical. Such chemicals include those:

- Brought directly into the workplace and handled, stored and used for processing e.g. solvents, cleaning agents, glues, resins, paints.
- Generated by a process or work activity e.g. fumes from welding/ soldering, dust from machining of wood, flour dust, solvents.
- Generated as waste or residue e.g. fumes from soldering iron, carbon monoxide from engine or motor exhausts.

4.1.2. How can chemicals be hazardous to health?

Chemicals can cause many different types of harm, ranging from mild skin irritation to cancer. The effects of hazardous chemicals may be seen:

- Immediately after contact (e.g. chemical burn) or many years after the exposure (e.g. lung cancer following exposure to asbestos).
- Following a single short exposure (e.g. infrequent use of a chemical) or longer-term exposures (e.g. daily use of a chemical in the workplace).

Therefore, it is important to minimise exposure to chemicals at all times.

- In order for a chemical to be hazardous to a person's health, it must either be in contact with or enter the body.
- Here are some examples of how chemicals can affect the body.

4.1.2.1. Effects on brain and nervous system

For example, exposure to pesticides, mercury, lead, solvents, carbon monoxide gas.

4.1.2.2. Eye, nose and throat irritation (dryness, soreness or pain)

For example, exposure to acid mists and vapours, welding fumes or diesel exhaust.

4.1.2.3. Effects on the lung (lung damage)

For example, asbestos (lung cancer), welding fume (chronic obstructive pulmonary disease).

4.1.2.4. Irritant induced asthma

For example, acids ("burn effect" on airways).

4.1.2.5. Allergic asthma

For example, flour dust, isocyanate, wood dust.

4.1.2.6. Liver damage

For example, exposure to vinyl chloride.

4.1.2.7. Bladder damage

For example, exposure to some azo dyes (bladder cancer).

4.1.2.8. Effects on skin

A. Allergic contact dermatitis

For example, nickel, latex, chromate (found in some cements).

B. Irritant contact dermatitis

For example, solvents, detergents, oils, lubricants.

C. Effects on blood and bone marrow

For example, exposure to benzene in petrol fumes (anaemia and leukaemia).

4.1.3. Health Effects of Chemical Exposure

4.1.3.1. Introduction

By their nature, the manufacture, storage, and transport of chemicals are accidents waiting to happen. Chemicals can be corrosive, toxic, and they may react, often explosively. The impacts of chemical accidents can be deadly, for both human beings and the environment.

Many if not most products we use in everyday life are made from chemicals and thousands of chemicals are used by manufacturing industries to make these products. The source of many of these chemicals is petroleum, which is refined into two main fractions: fuels and the chemical feedstocks that are the building blocks of plastics, paints, dyes, inks, polyester, and many of the products we buy and use every day. Fuels and chemical feedstocks made from petroleum are called organic chemicals. The other important class of chemicals is inorganics, which include acids, caustics, cyanide, and metals.

4.1.3.2. Terms

A. Occupational disease

Changing the worker's health as a result of exposure to harmful agents, habitual and continuous way, in place and working time.

B. Damage

Bodily injury, functional disorder or illness resulting, directly or indirectly work accident causing reduced ability to work, gain or death of the employee.

C. Safety Data Sheet

Document that identifies and characterizes chemical in terms of safety in transport, handling, storage and disposal (hazards / risks and preventive measures and intervention in fire, stroke, first aid ...).

D. Health at work

Its purpose is to promote global health of workers, adaptation to function and the prevention of exposure of harmful agents, habitual and continuous way, in place and working time.

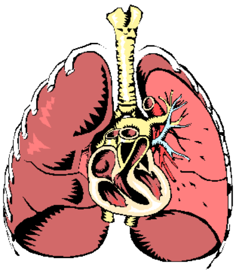
4.1.3.3. Exposure to chemical contaminants

Chemical agents are substances that are handled by the worker or generated throughout the production process, can be absorbed by the body and seriously harm health.

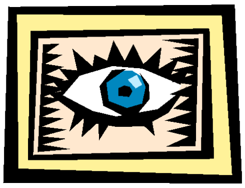
A. Routes of Exposure

There are four routes by which a substance can enter the body: inhalation, skin (or eye) absorption, ingestion, and injection.

A.1. Inhalation: For most chemicals in the form of vapours, gases, mists, or particulates, inhalation is the major route of entry. Once inhaled, chemicals are either exhaled or deposited in the respiratory tract. If deposited, damage can occur through direct contact with tissue or the chemical may diffuse into the blood through the lung-blood interface.

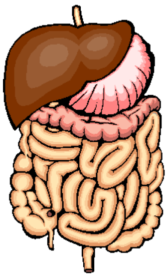


Upon contact with tissue in the upper respiratory tract or lungs, chemicals may cause health effects ranging from simple irritation to severe tissue destruction. Substances absorbed into the blood are circulated and distributed to organs that have an affinity for that particular chemical. Health effects can then occur in the organs, which are sensitive to the toxicant.



A.2. Skin (or eye) absorption: Skin (dermal) contact can cause effects that are relatively innocuous such as redness or mild dermatitis; more severe effects include destruction of skin tissue or other debilitating conditions. Many chemicals can also cross the skin barrier and be absorbed into the blood system. Once absorbed, they may produce systemic damage to internal organs. The eyes are particularly sensitive to chemicals. Even a short exposure can cause severe effects to the eyes or the substance can be absorbed through the eyes and be transported to other parts of the body causing harmful effects.

A.3. Ingestion: Chemicals that inadvertently get into the mouth and are swallowed do not generally harm the gastrointestinal tract itself unless they are irritating or corrosive.



Chemicals that are insoluble in the fluids of the gastrointestinal tract (stomach, small, and large intestines) are generally excreted. Others that are soluble are absorbed through the lining of the gastrointestinal tract. They are then transported by the blood to internal organs where they can cause damage.

A.4. Injection: Substances may enter the body if the skin is penetrated or punctured by contaminated objects. Effects can then occur as the substance is circulated in the blood and deposited in the target organs.

Once the chemical is absorbed into the body, three other processes are possible: metabolism, storage, and excretion. Many chemicals are metabolized or transformed via chemical reactions in the body. In some cases, chemicals are distributed and stored in specific organs. Storage may reduce metabolism and therefore, increase the persistence of the chemicals in the body. The various excretory mechanisms (exhaled breath, perspiration, urine, feces, or detoxification) rid the body, over a period of time, of the chemical. For some chemicals elimination may be a matter of days or months; for others, the elimination rate is so low that they may persist in the body fora lifetime and cause deleterious effects.

B. Toxic effects of chemical exposure

The health effects of hazardous chemicals are often less clear than the physical hazards. Data on the health effects of chemical exposure, especially from chronic exposure, are often incomplete. When discussing the health effects of chemicals, two terms are often used interchangeably - toxicity and hazard. However, the actual meanings of these words are quite different. Toxicity is an inherent property of a material, similar to its physical constants. It is the ability of a chemical substance to cause an undesirable effect in a biological system. Hazard is the likelihood that a material will exert its toxic effects under the conditions of use. Thus, with proper handling, highly toxic chemicals can be used safely. Conversely, less toxic chemicals can be extremely hazardous if handled improperly.

RISK = TOXICITY x EXPOSURE

The actual health risk of a chemical is a function of the toxicity and the actual exposure. No matter how toxic the material may be, there is little risk involved unless it enters the body. An assessment of the toxicity of the chemicals and the possible routes of entry will help determine what protective measures should be taken.

This is called chemical exposure. Although some chemical exposures are safe, others are not. A certain amount of a harmful chemical must enter your body to make you sick. Harmful chemicals can get into your body if you breathe, eat, or drink them or if they are absorbed through your skin.

People respond to chemical exposures in different ways. Some people may come into contact with a chemical and never be harmed. Others may be more sensitive and get sick. Sometimes illness happens only if you are exposed to a harmful substance for a long time.

Many factors play a part in whether you get sick from contact with chemicals, including:

- The kind of chemical you are exposed to,
- How much of the chemical you were in contact with?
- How long the contact lasted?
- How often you were exposed?
- How it entered your body? and
- Your health.

Toxicity can be defined as the relative ability of a substance to cause adverse effects in living organisms. This relative ability is dependent upon several conditions. The quantity or the dose of the substance determines whether the effects of the chemical are toxic, nontoxic or beneficial. In addition to dose, other factors may also influence the toxicity of the compound such as the route of entry, duration and frequency of exposure, variations between different species (interspecies) and variations among members of the same species (interspecies).

Exposure is defined as contact over time and space between a person and one or more chemical.

How a chemical exposure affects a person depends on many factors? The dose is the amount of a chemical that actually enters the body. The actual dose that a person receives depends on the concentration of the chemical and the frequency and duration of the exposure. The sum of all routes of exposure must be considered when determining the dose.

In addition to the dose, the outcome of exposure is determined by the way the chemical enters the body, the physical properties of the chemical, and the susceptibility of the individual receiving the dose.

4.1.3.4. The dose-response relationship

In general, a given amount of a toxic agent will elicit a given type and intensity of response. The dose-response relationship is a fundamental concept in toxicology and the basis for measurement of the relative harmfulness of a chemical. A dose-response relationship is defined as a consistent mathematical and biologically plausible correlation between the number of individuals responding and a given dose over an exposure period.

A. Dose terms. In toxicology, studies of the dose given to test organisms is expressed in terms of the quantity administered:

- **Quantity per unit mass (or weight)**. Usually expressed as milligram per kilogram of body weight (mg/kg).
- **Quantity per unit area of skin surface**. Usually expressed as milligram per square centimetre (mg/cm^2).

- **Volume of substance in air per unit volume of air**. Usually given as microliters of vapour or gas per litre of air by volume (ppm). Particulates and gases are also given as milligrams of material per cubic meter of air (mg/m3).

The period of time over which a dose has been administered is generally specified. For example, 5 mg/kg/3 D is 5 milligrams of chemical per kilogram of the subject's body weight administered over a period of three days. For dose to be meaningful it must be related to the effect it causes.

For example, 50 mg/kg of chemical "X" administered orally to female rats has no relevancy unless the effect of the dose, say sterility in all test subjects, is reported.

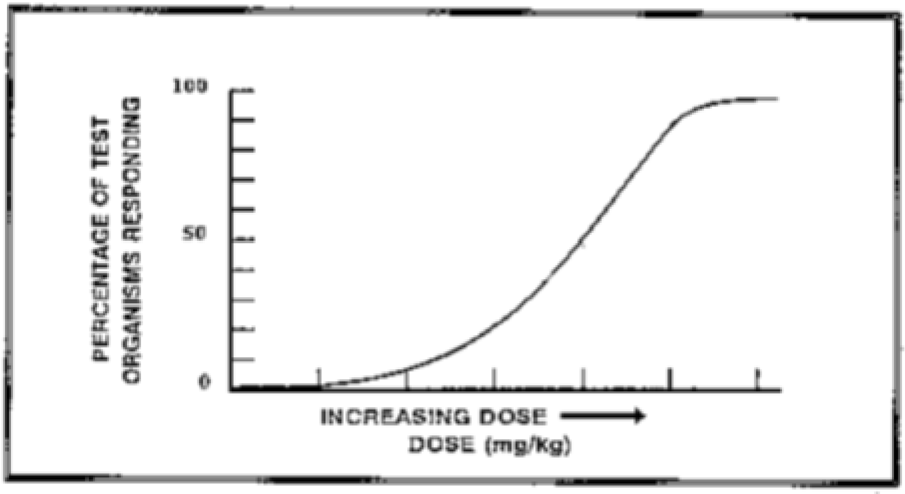
B. Dose-response curves. A dose-response relationship is represented by a dose-response curve.

The curve is generated by plotting the dose of the chemical versus the response in the test population. There are a number of ways to present this data. One of the more common methods for presenting the dose-response curve is shown in Figure.4.1. In this example, the dose is expressed in "mg/kg" and depicted on the "x" axis. The response is expressed as a "cumulative percentage" of animals in the test population that exhibits the specific health effect under study.

Values for "cumulative percentage" are indicated on the "y" axis of the graph. As the dose increases, the percentage of the affected population increases.

Dose-response curves provide valuable information regarding the potency of the compound.

Figure.4.1. Hypothetical dose-response curve.



C. Dose-response terms. The National Institute for Occupational Safety and Health (NIOSH) defines a number of general dose-response terms in the "Registry of Toxic Substances" (1983, p. xxxii).

C.1. Toxic dose low (TDLO): The lowest dose of a substance introduced by any route, other than inhalation, over any given period of time, and reported to produce any toxic effect in humans or to produce tumorigenic or reproductive effects in animals.

C.2. Toxic concentration low (TCLO): The lowest concentration of a substance in air to which humans or animals have been exposed for any given period of time that has produced any toxic effect in humans or produced tumorigenic or reproductive effects in animals.

C.3. Lethal dose low (LDLO): The lowest dose, other than LD50 of a substance introduced by any route, other than inhalation, which has been reported to have caused death in humans or animals.

C.4. Lethal dose fifty (LD50): A calculated dose of a substance which is expected to cause the death of 50 percent of an entire defined experimental animal population. It is determined from the exposure to the substance by any route other than inhalation.

C.5. Lethal concentration low (LCLO): The lowest concentration of a substance in air, other than LC50, which has been reported to cause death in humans or animals.

C.6. Lethal concentration fifty (LC50): A calculated concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50 percent of an entire defined experimental animal population.

D. Limitations of dose-response terms: Several limitations must be recognized when using dose response data. First, it is difficult to select a test species that will closely duplicate the human response to a specific chemical. For example, human data indicates that arsenic is a carcinogen, while animal studies do not demonstrate these results. Second, most lethal and toxic dose data are derived from acute (single dose, short-term) exposures rather than chronic (continuous, long term) exposures. A third shortcoming is that the LD50 or LC50 is a single value and does not indicate the toxic effects that may occur at different dose levels.

E. Factors influencing toxicity: Many factors affect the reaction of an organism to a toxic chemical. The specific response that is elicited by a given dose varies depending on the species being tested and variations that occur among individuals of the same species.

F. Duration and frequency of exposure: There is a difference in type and severity of effects depending on how rapidly the dose is received (duration) and how often the dose is received (frequency). Acute exposures are usually single incidents of relatively short duration--a minute to a few days. Chronic exposures involve frequent doses at relatively low levels over a period of time ranging from months to years.

If a dose is administered slowly so that the rate of elimination or the rate of detoxification keeps pace with intake, it is possible that no toxic response will occur. The same dose could produce an effect with rapid administration.

4.1.3.5. Classification of factors influencing toxicity

A. Routes of exposure: Biological results can be different for the same dose, depending on whether the chemical is inhaled, ingested, applied to the skin, or injected. Natural barriers impede the intake and distribution of material once in the body. These barriers can attenuate the toxic effects of the same dose of a chemical. The effectiveness of these barriers is partially dependent upon the route of entry of the chemical.

B. Interspecies variation: For the same dose received under identical conditions, the effects exhibited by different species may vary greatly. A dose which is lethal for one species may have no effect on another. Since the toxicological effects of chemicals on humans is usually based on animal studies, a test species must be selected that most closely approximates the physiological processes of humans.

C. Interspeciesvariations: Within a given species, not all members of the population respond to the same dose identically. Some members will be more sensitive to the chemical and elicit response at lower doses than the more resistant members which require larger doses for the same response.

D. Age and maturity: Infants and children are often more sensitive to toxic action than younger adults. Elderly persons have diminished physiological capabilities for the body to deal with toxic insult. These age groups may be more susceptible to toxic effects at relatively lower doses.

E. Gender and hormonal status: Some chemicals may be more toxic to one gender than the other. Certain chemicals can affect the reproductive system of either the male or female. Additionally, since women have a larger percentage of body fat than men, they may accumulate more fat-soluble chemicals. Some variations in response have also been shown to be related to physiological differences between males and females.

F. Genetic makeup: Genetic factors influence individual responses to toxic substances. If the necessary physiological processes are diminished or defective the natural body defences are impaired. For example, people lacking in the G6PD enzyme (a hereditary abnormality) are more likely to suffer red blood cell damage when given aspirin or certain antibiotics than persons with the normal form of the enzyme.

G. State of health: Persons with poor health are generally more susceptible to toxic damage due to the body's decreased capability to deal with chemical insult.

H. Environmental factors: Environmental factors may contribute to the response for a given chemical. For example, such factors as air pollution, workplace conditions, living conditions, personal habits, and previous chemical exposure may act in conjunction with other toxic mechanisms.

I. Chemical combinations: Some combinations of chemicals produce different effects from those attributed to each individually:

J. Synergists: chemicals that, when combined, cause a greater than additive effect.

For example, hepatotoxicity is enhanced as a result of exposure to both ethanol and carbon tetrachloride.

K. Potentiation: It is a type of synergism where the potentiator is not usually toxic in itself, but has the ability to increase the toxicity of other chemicals.

Type	**Example**
Factories related to the chemical	Composition 7 salt,freebase, etc.); physical characteristics (particle size, liquid, soils, etc.); physical properties (volatility, solubility, etc.); presence of impurities; break down products; carrier.
Factories related to	Dose; concentration; route of exposure (ingestion, skin absorption,

exposure	injection, inhalation); duration.
Factories related to person exposed	Heredity: immunology; nutrition; hormones; age; sex; health status; pre-existing diseases.
Factories related to environment	Carrie (air, water, food, soil); additional chemical present (synergism, antagonism); temperature: air pressure.

4.1.3.6. Health effects

Human health effects caused by exposure to toxic substances fall into two categories: short-term and long-term effects. Short-term effects (or acute effects) have a relatively quick onset (usually minutes to days) after brief exposures to relatively high concentrations of material (acute exposures). The effect may be local or systemic. Local effects occur at the site of contact between the toxicant and the body. This site is usually the skin or eyes, but includes the lungs if irritants are inhaled or the gastrointestinal tract if corrosives are ingested. Systemic effects are those that occur if the toxicant has been absorbed into the body from its initial contact point, transported to other parts of the body, and cause adverse effects in susceptible organs. Many chemicals can cause both local and systemic effects.

Long-term effects (or **chronic effects**) are those with a long period of time (years) between exposure and injury. These effects may occur after apparent recovery from acute exposure or as a result of repeated exposures to low concentrations of materials over a period of years (chronic exposure).

Health effects manifested from acute or chronic exposure are dependent upon the chemical involved and the organ it effects. Most chemicals do not exhibit the same degree of toxicity for all organs.

Usually the major effects of a chemical will be expressed in one or two organs. These organs are known as target organs which are more sensitive to that particular chemical than other organs.

- **Respiratory tract:** The respiratory tract is the only organ system with vital functional elements in constant, direct contact-with the environment. The lung also has the largest exposed surface area of any organ on a surface area of 70 to 100 square meters versus 2 square meters for the skin and 10 square meters for the digestive system.

The toxicants can be classified according to how they affect the respiratory tract.

- **Asphyxiants**: gases that deprive the body tissues of oxygen
- **Simple asphyxiants** are physiologically inert gases that at high concentrations displace air leading to suffocation. Examples: nitrogen, helium, methane, neon, argon.
- **Chemical asphyxiants** are gases that prevent the tissues from getting enough oxygen.
- **Examples:** carbon monoxide and cyanide. Carbon monoxide binds to haemoglobin 200 times more readily than oxygen. Cyanide prevents the transfer of oxygen from blood to tissues by inhibiting the necessary transfer enzymes.
- **Irritants**: chemicals that irritate the air passages. Constriction of the airways occurs and may lead to edema (liquid in the lungs) and infection. Examples: hydrogen fluoride, chlorine, hydrogen chloride, and ammonia.
- **Necrosis producers**: Chemicals that result in cell death and edema. Examples: ozone and nitrogen dioxide.
- **Fibrosis producers**: Chemicals that produce fibrotic tissue which, if massive, blocks airways and decreases lung capacity. Examples: silicates, asbestos, and beryllium.
- **Allergens**: Chemicals that induce an allergic response characterized bybronchoconstriction and pulmonary disease. Examples: isocyanates and sulphur dioxide.
- **Carcinogens**: Chemicals that are associated with lung cancer. Examples: cigarette smoke, coke oven emissions, asbestos, and arsenic.

Not only can various chemicals affect the respiratory tract, but the tract is also a route for chemicals to reach other organs. Solvents, such as benzene and tetrachloroethane, anaesthetic gases, and many other chemical compounds can be absorbed through the respiratory tract and cause systemic effects.

4.1.3.7. Preventative measures include

A. Engineering controls (isolating or removing the hazard):

- Enclose process,
- Provide local exhaust

B. Administrative practices

- Time work so fewer workers are exposed,
- Work upwind of mixing operations,
- Shower after shift
- Change clothes
- No food or smoking in work areas

C. Personal protective equipment

C.1. Eye protection

Depending on the job you are doing and the type of material you are handling, you may need various levels of eye protection (e.g. safety glasses, chemical safety goggles, a face shield or some combination of these).

C.2. Skin protection

Skin protection includes items such as gloves, aprons, full body suits, and boots. The MSDS should tell you the types of materials that provide the best protection against the product you are using. No one material acts as a barrier to all chemicals. It is also important to consider the temperature conditions and the need for materials not easily cut or torn.

C.3. Respiratory protection

There are several types of respirators on the market. Some are effective against some chemicals but may provide little or no protection against others. Selecting the best respirator for you can be quite complicated.

A qualified person must carry out a detailed assessment of the workplace, including all chemicals used and their airborne concentrations and forms. Consequently, complete respiratory protection guidelines generally cannot be given on the MSDS. If respirators are required at your work site, a complete respiratory protection program including respirator selection, fit testing, training and maintenance is necessary. Levitt-Safety's | EHS Training & Consulting department can provide all of these services – call us today for more information.

4.1.4. Steps to chemical safety

You have seen how chemicals effect the body. There are four ways chemicals can enter the body:

- Inhalation: Breathing in contaminated air is the most common way that workplace chemicals enter the body.
- Contact with the skin or eyes: Some chemicals can damage the skin or eyes (e.g. irritation) or pass through the skin into the body.
- Ingestion: Workplace chemicals may be swallowed accidentally if food or hands are contaminated.
- Injection: Injection can occur when a sharp object (e.g. needle) punctures the skin and injects a chemical directly into the bloodstream.

Here are some terms that explain the health effects of exposure to chemicals.

Table.4.1. The health effects of exposure to chemicals.

Term	**What this means to you**
Acute toxicity	An adverse health effect following a single exposure to a chemical (e.g. skin contact with insecticides, accidental ingestion of a chemical).
Reproductive toxin **Respiratory sensitizers** **Skin sensitizers** **Carcinogen**	A chemical that causes or can potentially cause cancer (e.g. breathing in asbestos fibres, skin contact with used motor oils).
Chronic toxicity	An adverse health effect following repeated exposure to a chemical, which can occur following a relatively short exposure (e.g. weeks) or longer term exposure (e.g. years).
CMR	A chemical that is Carcinogenic, Mutagenic or Toxic to Reproduction.
Corrosive	A chemical that causes irreversible damage to skin, eyes or airways (e.g. strong acids and strong bases such as concentrated hydrochloric acid or concentrated

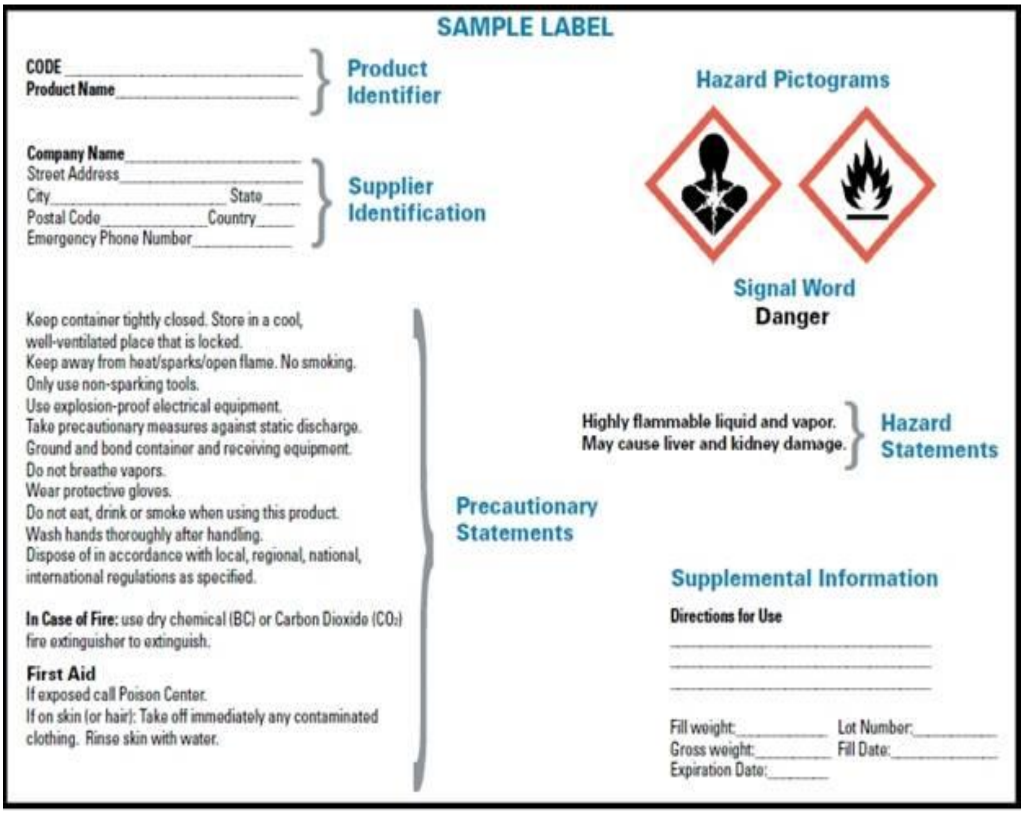
	hydroxides).
Irritant	A chemical that causes reversible damage to skin, eyes or airways (e.g. detergents or soaps).
Mutagen	A chemical that can cause permanent damage to genetic material in cells, which can possibly lead to heritable genetic damage or cancer (e.g. UV rays from the sun, benzene).

4.1.5. Where can you find information about chemical hazards?

The most important sources of information on the hazards of your chemicals are the label and the Safety Data Sheet (SDS).

Chemicals should be supplied with a label attached to the container. The label gives information on the chemical or product name, the chemical hazards and the precautions you should take into account to ensure safe use.

Figure.4.2. Sample label.



SAMPLE LABEL

CODE ________
Product Name ________

Company Name ________
Street Address ________
City ________ State ____
Postal Code ________ Country ____
Emergency Phone Number ________

Keep container tightly closed. Store in a cool, well-ventilated place that is locked.
Keep away from heat/sparks/open flame. No smoking.
Only use non-sparking tools.
Use explosion-proof electrical equipment.
Take precautionary measures against static discharge.
Ground and bond container and receiving equipment.
Do not breathe vapors.
Wear protective gloves.
Do not eat, drink or smoke when using this product.
Wash hands thoroughly after handling.
Dispose of in accordance with local, regional, national, international regulations as specified.

In Case of Fire: use dry chemical (BC) or Carbon Dioxide (CO_2) fire extinguisher to extinguish.

First Aid
If exposed call Poison Center.
If on skin (or hair): Take off immediately any contaminated clothing. Rinse skin with water.

Danger

Highly flammable liquid and vapor.
May cause liver and kidney damage.

Directions for Use
____
____
____

Fill weight: ________ Lot Number: ________
Gross weight: ________ Fill Date: ________
Expiration Date: ________

Figure.4.3. Compliant label (For a GHS).

Wash hands thoroughly after handling. Keep container tightly closed when not in use Keep away from heat, sparks and open flames - may explode when exposed to high heat. Use in an open area that is well-ventilated. Breathing in ammonia is irritating and corrosive. Wear protective gloves and safety goggles to prevent burns and irritation.

If swallowed: Immediately call Poison Control or doctor/physician. Drink water or milk to dilute ammonia.

See Safety Data Sheet (SDS) for further details regarding safe use of this product.

ABC Chemicals - 123 Main Street - Cincinnati, OH - www.abcchem.com - 800-733-5252

4.1.6. Safety Data Sheets (SDS)

You must have a SDS for each hazardous chemical that you use. If you don’t, contact the supplier, who is required to give you one. You should keep your SDSs in a clearly identified place where they can be easily accessed by your employees and by emergency services - they will require these sheets when they attend a chemical incident.

You should make sure all your employees know where the SDSs are stored and that they have read and understood them, if required.

Safety data sheets must (Seen to annexes for sample safety data sheet);

- Be provided for chemicals classified as hazardous.
- Contain 16 headings.
- Be prepared by a competent person.
- Be specific to the chemical.
- Be clear and understandable.
- Be provided free of charge.
- Be provided no later than at the time of first delivery.
- Be provided upon update or revision to everyone who has received the chemical during the previous 12 months.
- Be dated and the pages numbered.

Table.4.2. Headings on Safety Data Sheets.

Safety data sheets must contain the following headings		
1. Identification of the substance/preparation and of the company/ undertaking. 2. Hazards identification. 3. Composition/ information on ingredients. 4. First aid measures. 5. Fire-fighting measures.	6. Accidental release measures. 7. Handling and storage. 8. Exposure controls/ personal protection. 9. Physical and chemical properties. 10. Stability and reactivity. 11. Toxicological information.	12. Ecological information. 13. Disposal consideration. 14. Transport information. 15. Regulatory information. 16. Other information.

The SDS plays a number of roles in managing the safe use of chemicals in your workplace:

- It ensures the product is being used as intended by the manufacturer or importer.
- It is a key tool for risk assessment as it includes detailed hazard information.
- It provides options for appropriate controls measures and procedures to be applied.
- Sufficient information should be provided to select the necessary Personal Protective Equipment (PPE) and to develop necessary emergency procedures.
- It may be used as the basis of a training program for workers as it covers hazards, information on safe handling and storage and emergency procedures.
- Workplace monitoring and health surveillance strategies may often be based on advice contained in the SDS.

4.1.7. Make a list of all the chemicals in your workplace

Before you can identify the chemical hazards in your workplace, you first need to identify the chemicals which you store or use, and the processes which generate dusts or fumes.

You can do this by walking through your workplace and making a note of the chemicals or processes you see. You can also ask your employees to help you identify chemicals which they use or are aware of. Remember: chemicals can be individual substances (e.g. acetone or petrol) or mixtures / products (e.g. paint or degreasers).

You may find it useful to record this information in a Chemical Inventory. A sample Chemical Inventory template is included in the appendix of this document.

The following are some tips on preparing a chemical inventory.

4.1.8. Clearly identify each chemical

Check the label on the container, the safety data sheet (SDS) or any documentation which came with the chemical to help identify it. You can request a SDS from your supplier if you don’t have one available.

These may be chemicals where the label is no longer visible or attached to the container, or where chemicals are stored in an unmarked container. It is never safe to use chemicals if you are not sure what they are! It is important to include such “unknowns” on your inventory sheet so that their location is documented. You should arrange to have these unknown chemicals safely removed from your workplace.

It is good practice to only store the amount of chemical you need. By indicating on your inventory where the chemical is stored you can easily locate it and also avoid storing extra amounts. You can also note the type of container it is stored in (e.g. plastic or glass bottle) and the condition of the container.

The label and SDS are the most important sources of information about the hazardous properties of your chemicals, so it is important that you have an up to date SDS for each chemical and that the label attached to the chemical container is visible.

Some chemical hazards don’t have a hazard pictogram or symbol associated with them so it is important to read all the hazard information on the label or in the SDS to get an overview of the hazardous properties.

4.1.9. Have you assessed the exposure to the chemical?

Once you have identified your chemicals and their hazards, you then need to assess what the potential exposure to the chemical is.

An exposure assessment involves looking at each chemical which you have identified and considering the following questions:

Table.4.3. Potentially exposure assessment.

How you are using the chemical?	**Potentially lower exposure**	**Potentially higher exposure**
Who uses the chemical? (e.g. how many people?)	A limited number of authorised personnel only.	Anyone can use this chemical.
How long is each user exposed to the chemical? (e.g. full shift or a few minutes?)	Personnel are only exposed for short durations.	Chemical is part of the work activity and personnel are exposed throughout the full shift.
How often is the chemical used?	Chemical is used infrequently.	Chemical is in continuous use.
How is the chemical used? (e.g. sprayed, poured?)	Chemical is poured, therefore less likely to be breathed in during use.	Chemical is sprayed and therefore is more likely to be breathed in.
How will the user be exposed? (e.g. breathing it in, contact with skin?)	Effect of exposure will depend on the nature of the chemical. Refer to SDS.	Effect of exposure will depend on the nature of the chemical. Refer to SDS.
How much is used?	Small quantities are used.	Bulk quantities of the chemical are used.
Can non-users be exposed? (e.g. people working near the task, visitors, cleaning or maintenance staff?)	Only trained/authorised personnel are exposed to the chemical.	Chemical is used in general areas where all personnel are exposed.

Once you have identified your chemical hazards and considered the exposure to them, you then need to assess the risk for each.

4.1.10. Assessing the risk involves

Evaluating the information on the hazards and uses (potential exposure) of the chemical.

Considering the likelihood of being exposed to a hazard and the severity of that hazard, which may lead to an adverse effect on health or safety.

4.2. Environmental impacts

4.2.1. Objective of the course

The objective of this course is to give information about the environmental impacts of chemical accidents. Main focus is on the methodology of impact assessment.

Many figures are quoted for the number of chemical substances in common use today, and for the number of new ones introduced every year. Probably reliable are the values at the figure of 60000 chemicals in use with several thousand additional ones being added annually [3].

Initially, it might seem that such numbers render impossible the task of identifying priority chemicals as potential environmental hazards, at least on anything but an intuitive basis. However, such attempts have been made and, although the earlier studies were largely overwhelmed by the data required and ended up using very simple sets of attributes as the basis for priority identification, the experience gained has increased our understanding of what is necessary. Today, large data banks are being organized for precisely this purpose, most notably by the International Registry for Potentially Toxic Chemicals, an activity of UNEP [3].

As a rule, it is necessary to know certain quite specific attributes about a chemical substance to predict whether it will be a danger to the environment in general. It must be released in large quantities; it must persist in the ecosystem it enters (or be transformed into an equally or more seriously toxic material); and it must find its way to target organisms by having some kind of affinity for biological materials. Also, of course, it must be in some sense toxic. This chapter surveys briefly what is known about these various steps, and looks at how we can arrive at a useful analysis of which chemicals ought to be of primary concern [3].

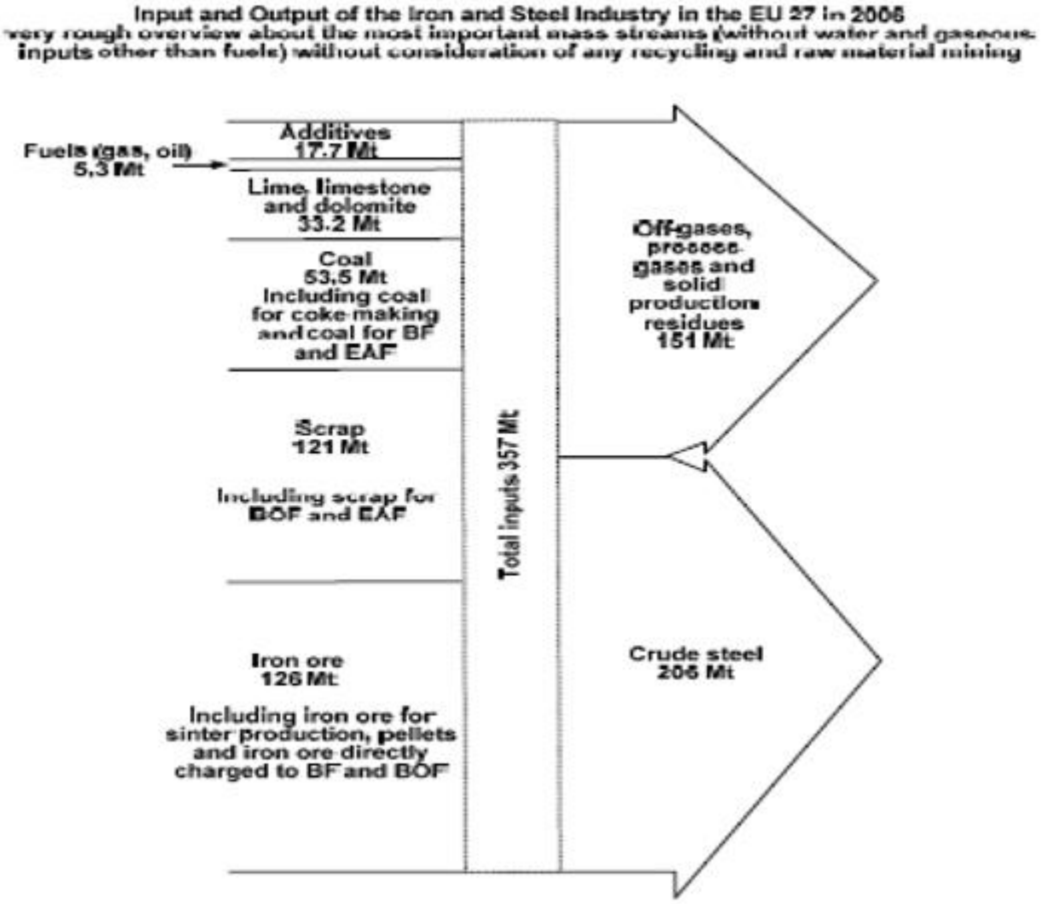
4.2.2. Identification of the course

Characteristics of Iron and Steel Industry and identification of the main environmental aspect by sub- processes are described as follows basing on reference source /12/.

The iron and steel industry is highly intensive in both materials and energy. The figure presents a simplified input/output scheme illustrating and numbering the most important mass streams together with the quantity of crude steel produced in the EU-27 in 2006. The overview does not include raw material mining, water and gaseous inputs other than fuels and recycling activities.

The figure 4.4. illustrates that almost half of the input ends up as off-gases, process gases and solid production residues.

Figure.4.4. Overview of the inputs and outputs for the manufacture of iron and steel (best available techniques reference document for iron and steel production, European Commission 2013).



Following the two most important steelmaking process routes via the sinter/pellet plant/coke oven/blast furnace/basic oxygen converter and the electric arc furnace, the key environmental issues for action in response to environmental concerns can be summarized below:

4.2.2.1. Sinter plants

Sinter, as a product of an agglomeration process of materials which contain iron, represents a major part of the burden of blast furnaces. The main stack emissions of sinter plants account for up to 50 % of the total dust emissions from an integrated steelwork. Other relevant pollutants in the off-gas emissions from the sinter strand and the cooler are heavy metals, SO2, HCl, HF, PAH and persistent organic pollutants (such as PCB and PCDD/F). Furthermore, the recovery of sensible heat and the utilisation of solid wastes are severe issues. Environmental benefits are linked to this process with the recycling of iron-rich solid by-products of downstream processes and the potential for heat recovery.

4.2.2.2. Palletisation plants

Palletisation is another process used to agglomerate materials which contain iron where emissions to air dominate the environmental issues. Other main issues in pellet plants are the use of sensible heat, the treatment of waste water and the internal utilisation of process residues.

4.2.2.3. Coke oven plants

A coke plant consists of one or more coke oven batteries with a coke oven firing system (under firing) and the process gas treatment unit where emissions to air are the most significant. The main point source for emissions to air is the waste gas from under firing. Additionally, many of the emissions are diffuse emissions from various sources such as the unloading, storage, handling, crushing and blending (preparation) of coal, the leakages from lids and adherences onto frames, oven and leveller doors, the ascension pipes and charging holes of coal into and the pushing of coke out of the chambers, and finally, coke quenching and coke grading (crushing and screening), transport, handling and storage. Diffuse/fugitive VOC emissions to air can occur from coke oven batteries and diffuse/fugitive ammonia and BTX emissions from by-products plants which all have the potential to create odour nuisances. Dust and SO2 emissions at coke oven plants and other plants where coke oven gas is used as a fuel is a concern.

Thus the desulphurisation of coke oven gas is a measure of high priority for minimising these emissions.

Waste water disposal is another major issue for coke oven plants. Optimised management of coke oven gas and its use in other processes of integrated plants allow energy savings and minimise air emissions.

4.2.2.4. Blast furnace plants

Significant emissions to all media occur where the blast furnace process for producing hot metals from materials which contain iron are used. Because of the high input of reducing agents (mainly coke and coal), this process consumes most of the overall energy input of an integrated steelwork. Relevant emissions to all media occur and these are described in detail. The main environmental issues are dust, waste water from blast furnace gas scrubbing, emissions from slag treatment such as SO2 and H2S which can lead to odour nuisances, dusts and sludge, and finally, the minimisation of energy consumption.

4.2.2.5. Basic oxygen furnace plants

Emissions to air from various sources such as primary and secondary dedusting, hot metal pre-treatment and secondary steelmaking and various solid process residues are the main environmental issues in oxygen steelmaking. In addition, waste water arises from wet dedusting (when applied) and from continuous casting. Particular attention should be paid to diffuse dust emissions which occur when secondary emission collecting systems are insufficient.

4.2.2.6. Electric arc furnace plants

The direct smelting of materials which contain iron (mainly scrap) is usually performed in electric arc furnaces which need considerable amounts of electrical energy and causes substantial emissions to air and solid process residues such as wastes and by-products (mainly filter dust and slag). The emissions to air from the furnace consist of a wide range of inorganic compounds (iron oxide dust and heavy metals) and organic compounds such as persistent organic pollutants (e.g. PCB and PCDD/F).

4.2.3. Outcome of the course

The principles of environmental impacts will be the core outcome of the course. the explanation below bases on references [1-2].

Entries into the environment which have been seen to cause considerable damage can be classified into three categories, depending on their geographical extent: point spills, chronic local releases and widespread releases.

By point spills we mean occasions when a significant amount of a chemical has entered an ecosystem at a point (in both space and time) and effects of contamination are expected in a well-defined more or less local area. The assumption is that the substance does not rapidly diffuse away, but remains in the immediate vicinity at a noticeably high concentration (or perhaps moves, but in such a way that levels remain high as it moves).

Such cases would normally occur when large quantities of a substance were being stored, transported or otherwise handled in concentrated form. This kind of situation would probably involve the commercial handling of an industrial chemical or fuel, and would include oil spills, leaks or spills of chlorine or other gases, PCBs, acids and so forth.

The fact is that we have a considerable amount of experience in dealing with such situation; authorities such as Transport Ministries and the Coast Guard or related services have recognized and planned for certain dangers for many years. Lists have been drawn up in most countries of those regarded as most hazardous. For substances in this category, assessment of toxic effects is a matter of record, and policy is typically directed towards emergency procedures to be followed in case of spills.

Chronic local releases are cases in which discharges have taken place over such periods of time, and in such quantities, that a larger region (for example, a river system, a catchment basin or the landscape downwind of a source) has been contaminated. This type of situation usually results from, or is associated with, a large industrial or municipal source. The effluent may be a general loading of organic material or a noxious gas, in which case the problem is simply that the ecosystem cannot incorporate such quantities as it gets, or it may be the release of much smaller quantities of much more toxic trace elements.

Thus, a single industrial source might produce both types of problem, by releasing organic waste material and at the same time discharging trace amounts of heavy metals. Similarly, an agricultural system might load an ecosystem with organic materials and at the same time release significant quantities of pesticides.

Either one, however, would still constitute a case of chronic local release of a damaging substance.

Such cases are the most numerous today, and are rather difficult to further classify. Attempts have been made to identify the kinds of releases most likely to be found in this category, and typically result in the following as the most important:

1. General nutrient discharge, leading to eutrophication.

2. The class of chemical generally referred to (somewhat inaccurately) as heavy metals, and their organic derivatives in particular.

3. Manufactured organics known (and intended) to be toxic, specifically the pesticides.

4. The acidifying gases, oxides of sulphur and nitrogen.

The most serious type of entry is a widespread release, by which we mean release of a substance in sufficient quantity, and over a wide enough area, that there could result a noticeable pollution of a significant part of the entire earth's surface. If this should happen at a level at which the ecosystem itself was affected, the problem would be grave indeed, particularly so if the substance originated with an activity which was very widespread (so that the sources of pollution are many) and was associated with an activity on which many other activities depend (such as basic energy generation). And this is not to be assumed impossible; there are something like a thousand substances manufactured in such quantities as to be capable of polluting the entire globe, and there are many others which are released inadvertently as by-products of widespread operations.

It is important to distinguish those cases in which the ecosystems involved may be affected, as opposed to cases in which all that can be said is that the substance is detectable (sometimes only by extremely delicate instrumentation) in far-flung locations. The latter, obviously, may attract considerable attention but are not necessarily a problem. The former is so potentially serious that, if they should happen, we may already be too late to save some valued part of the environment.

It is instructive to examine those cases known so far in which truly global pollution has been recognized. There are at least six: radioactive fallout; DDT; PCBs; freons and similar fluorinated hydrocarbons; and, more recently, production of carbon dioxide; and, of course, the oxides of Sulphur and nitrogen and their end-product, acid rain.

The first three of these have not affected the structure and function of the ecosystem itself, only of certain targets in it (albeit rather important ones). The others, however, are very much of a threat to the more general system: freons and CO2 by changing the physical parameters to which all organisms must adjust (radiation level and temperature, respectively); while acid rain has been clearly seen to be overtly toxic to ecosystems, particular aquatic systems, over a wide geographical area. It is in this area that potential dangers are greatest and advance warning would seem to be most urgent.

It should be explicitly mentioned here that there is considerable dispute about some of these cases. While each one certainly represents a situation in which an unnatural chemical substance has been discharged into the environment, it does not at all follow that the environment itself has in some sense ended up with deleterious damage. In the case of radioactivity, for example, only in very local areas (detonation points) or experimental setups (the gamma forest) has there been a marked effect on the ecosystem generally. Ecologists have had to search with great care and tenacity to discover whether DOT residues were affecting ecosystems, in spite of the obvious fact that concentrations in the fat of certain mammals were enormous. The long-term effects of PCBs, at very low concentrations, remain a matter of debate.

The cases of freons and CO^2 are interesting in quite a different sense. These substances have clearly not had an adverse effect on the ecosystems exposed to them. However, on the basis of certain modelling studies and theoretical exercises, it became clear to some-and not to others-that a danger was present and would become real if action were not taken straight away. This is another profoundly important issue. If we wait until deleterious effects can be clearly demonstrated, remedial measures will be impossible. This means that, with a threat such as CO^2 production, we must consider the risk of a situation that has never occurred, and for which historical fact, the only convincing argument for many people, cannot even in theory be available. Nonetheless, as we become increasingly capable of poisoning our own environment, we must be prepared to depend on such theoretical arguments and models as are available to assess the consequences of particular policies. It is not a comfortable situation.

A further category might be added to our three kinds of spills or discharges, but as yet little is known about the possible dynamics and there are few examples to examine. This is the situation in which a substance may be quite dilute in the environment, but be concentrated geographically as well as in particular organisms (as opposed to simple bio magnification in a particular food chain, a phenomenon which we reasonably well understand). A possible case could arise from the dumping in the deep ocean of radioactive wastes. Escaped radioactivity might concentrate in fish which then congregate near the shore or even migrate to particular areas, thus constituting a source of radioactivity for a target, perhaps man. However, in such cases it is not usually assumed that a threat to the ecosystem generally exists, only that an unsuspected pathway to man might exist. Since only the former is the thrust of the present work, such cases are not discussed further.

For getting an overview about environmental impacts of an environmental accident, look an example description from Finland: Example case of environmental disaster in Finland: Talvivaara minehttp://www.nuclear-heritage.net/index.php/Talvivaara_mine:_environmental_disaster_in_Finland

4.2.4. Classification

The environmental impacts can be classified f.ex. into the following categories, widely used f.ex. applying life cycle assessment of products [1-2].

4.2.4.1. Abiotic resources depletion

Abiotic resources are non-living natural resources such as iron ore, crude oil, etc.

4.2.4.2. Acidification

The acidification potential of a pollutant is the tendency of that chemical to form the acidifying H+ ions. The Acidification Potential (AP) is expressed relative to the acidifying effect of SO2. NOx and SOx emissions from electricity production are common sources of acidification in the environment. These gases are released into the atmosphere where they are converted to nitric acid (HNO3) and sulphuric acid (H2SO4) respectively. The acids are spread to land and water, often as acid rain. Acid rain damages vegetation and built infrastructure, and acidification of surface waters have consequences for many aquatic species.

4.2.4.3. Eutrophication

Eutrophication is the most widespread environmental problems of water sources. It is due to the unnatural enrichment with plant nutrients, phosphorus and nitrogen. It increases the growth of microscopic plants, algae, and forms the dense mats of larger floating plants which result in the oxygen depletion and affects all the living organisms. The algae sink to the bottom and are broken down consuming oxygen in the bottom layer. If fresh oxygen-rich water from the surface does not reach the bottom layers, the oxygen concentration near the bottom will gradually be reduced until the bottom-dwelling organisms move away or die.

4.2.4.4. Global warming

To maintain the global energy balance, the earth atmosphere absorbs solar radiation and re-radiates this energy to space as infrared or longwave radiation. The atmosphere absorbs and emits longwave radiation, but as the atmosphere absorbs and emits the longwave radiation, but as the atmosphere is colder than the surface, it absorbs more energy than it emits to space. The energy that escapes to space is significantly smaller than that emitted by the surface. The difference, the energy trapped in the atmosphere is the greenhouse effect.

The major greenhouses gases are methane (CH4) and CO^2, both of which come from the generation of electricity, in transportation, burning of the fossil fuels and production of the plastic material. Because methane is 21 times more effective greenhouse gas than carbon dioxide, according to the United Nations Convention Framework on Climate Change, methane emissions were converted into CO2 equivalents in order to better represent the combined impact of both gases. The Global Warming Potential (GWP) is the potential contribution of a substance to the greenhouse effect. GWP for greenhouse gases are expressed as CO^2-equivalents, (CO^2-eq.) i.e. the effects are expressed relatively to the effect of CO^2. The potential greenhouse effect of a product/process can be estimated by calculating the product of the amount of emitted greenhouse gas per functional unit and the potential for greenhouse effect given in kg CO^2-equivalents per kg emitted gas.

4.2.4.5. Ozone layer depletion

Ozone Depletion Potential (ODP) values have been established mainly for hydrocarbons containing combined bromine, fluorine, and chlorine, or CFCs. The ozone layer is the naturally occurring belt of ozone gas on the earth’s atmosphere which serves as a shield from harmful ultraviolet radiation emitted by the sun. Due to the release of the pollution containing the chemicals Chlorine and Bromine, the ozone layer is deteriorating which allows a large amount of the UV-B rays to reach the earth causing skin cancer and cataracts in humans and harming animals.

4.2.4.6. Photochemical oxidant formation

Photochemical Ozone Creation Potential (POCP), also known as summer smog potential, measured in kg C2H4 equivalent, is a measure of how much a unit mass of a substance, contributes to the formation of ground level (tropospheric) ozone in the presence of UV radiation. The human and eco toxic pollution of the ground-level atmospheric layers caused by this is also called summer smog. Summer smog affects respiratory organs and has a harmful effect on plants and animals.

4.2.4.7. Oxygen demand and nitrification of water ecosystem

The organic material breaks down naturally by bacteria. It consumes oxygen and cause a lack of oxygen and makes it difficult for higher animal's vital signs. Lack of oxygen in bottom sediment release of nutrients, namely nitrogen and phosphorus in water. This phenomenon is known as internal loading. It increases eutrophication and it is still ultimately lead to oxygen wear, when plants die and are decomposed by bacteria.

4.2.5. Operation

Main Laws dealing with environmental protection are described below.

Integrated pollution prevention and control Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control [10].

Directive (“the IPPC Directive”) requires industrial and agricultural activities with a high pollution potential to have a permit. This permit can only be issued if certain environmental conditions are met, so that the companies themselves bear responsibility for preventing and reducing any pollution they may cause.

4.2.5.1. Mandatory environmental conditions

In order to receive a permit an industrial or agricultural installation must comply with certain basic obligations. In particular, it must:

Use all appropriate pollution-prevention measures, namely the best available techniques (which produce the least waste, use less hazardous substances, enable the substances generated to be recovered and recycled, etc.);

- prevent all large-scale pollution;
- prevent, recycle or dispose of waste in the least polluting way possible;
- use energy efficiently;
- ensure accident prevention and damage limitation;
- return sites to their original state when the activity is over.

In addition, the decision to issue a permit must contain a number of specific requirements, including:

- emission limit values for polluting substances (with the exception of greenhouse gases if the emission trading scheme applies - see below);
- any soil, water and air protection measures required;
- waste management measures;
- measures to be taken in exceptional circumstances (leaks, malfunctions, temporary or permanent stoppages, etc.);
- minimisation of long-distance or transboundary pollution;
- release monitoring;
- all other appropriate measures.

In order to coordinate the permit process required under the Directive and the greenhouse gas emission trading scheme, a permit issued in compliance with the Directive is not obliged to contain the emission limit values for greenhouse gases if these gases are subject to an emission trading scheme, provided there is no local pollution problem. The competent authorities can also decide not to impose energy efficiency measures targeted at combustion plants.

4.2.5.2. Permit applications

All permit applications must be sent to the competent authority of the Member State concerned, which will then decide whether or not to authorise the activity. Applications must include information on the following points:

a description of the installation and the nature and scale of its activities as well as its site conditions;

- the materials, substances and energy used or generated;
- the sources of emissions from the installation, and the nature and quantities of foreseeable emissions into each medium, as well as their effects on the environment;
- the proposed technology and other techniques for preventing or reducing emissions from the installation;
- measures for the prevention and recovery of waste;
- measures planned to monitor emissions;
- possible alternative solutions.

Without infringing the rules and practice of commercial and industrial secrecy, this information must be made available to interested parties:

- the public, using the appropriate means (including electronically) and at the same time as information concerning the procedure for licensing the activity, the contact details of the authority responsible for authorising or rejecting the project and the possibility for the public to take part in the licensing process;
- the other Member States, if the project is likely to have cross-border effects. Each Member State must submit this information to interested parties in its territory so that they can give their opinion.

Sufficient time must be allowed for all interested parties to react. Their opinions must be taken into account in the licensing procedure.

4.2.5.3. Administrative and monitoring measures

The decision to license or reject a project, the arguments on which this decision is based and possible measures to reduce the negative impact of the project must be made public and sent to the other Member States concerned. The Member States must, in accordance with their relevant national legislation, make provision for interested parties to challenge this decision in the courts.

The Member States are responsible for inspecting industrial installations and ensuring they comply with the Directive. An exchange of information on best available techniques (serving as a basis for setting emission limit values) is held regularly between the Commission, the Member States and the industries concerned. Reports on the implementation of the Directive are drawn up every three years.

The EU Directive of Environmental Impact Assessment [11] is in force since 1985 and applies to a wide range of defined public and private projects. The EIA procedure can be summarized as follows: the developer may request the competent authority to say what should be covered by the EIA information to be provided by the developer (scoping stage); the developer must provide information on the environmental impact (EIA report); the environmental authorities and the public (and affected Member States) must be informed and consulted; the competent authority decides, taken into consideration the results of consultations. The public is informed of the decision afterwards and can challenge the decision before the courts.

4.2.6. Emission, distribution, transport and transformation

A good deal of information is now available about how chemicals distributethemselves, move (or get moved) and change their chemical form in theenvironment. Furthermore, we know how to predict at least some of this behaviour using knowledge of physical and chemical properties and, recently, automated computer models of such behaviour have been developed and are gaining acceptance.

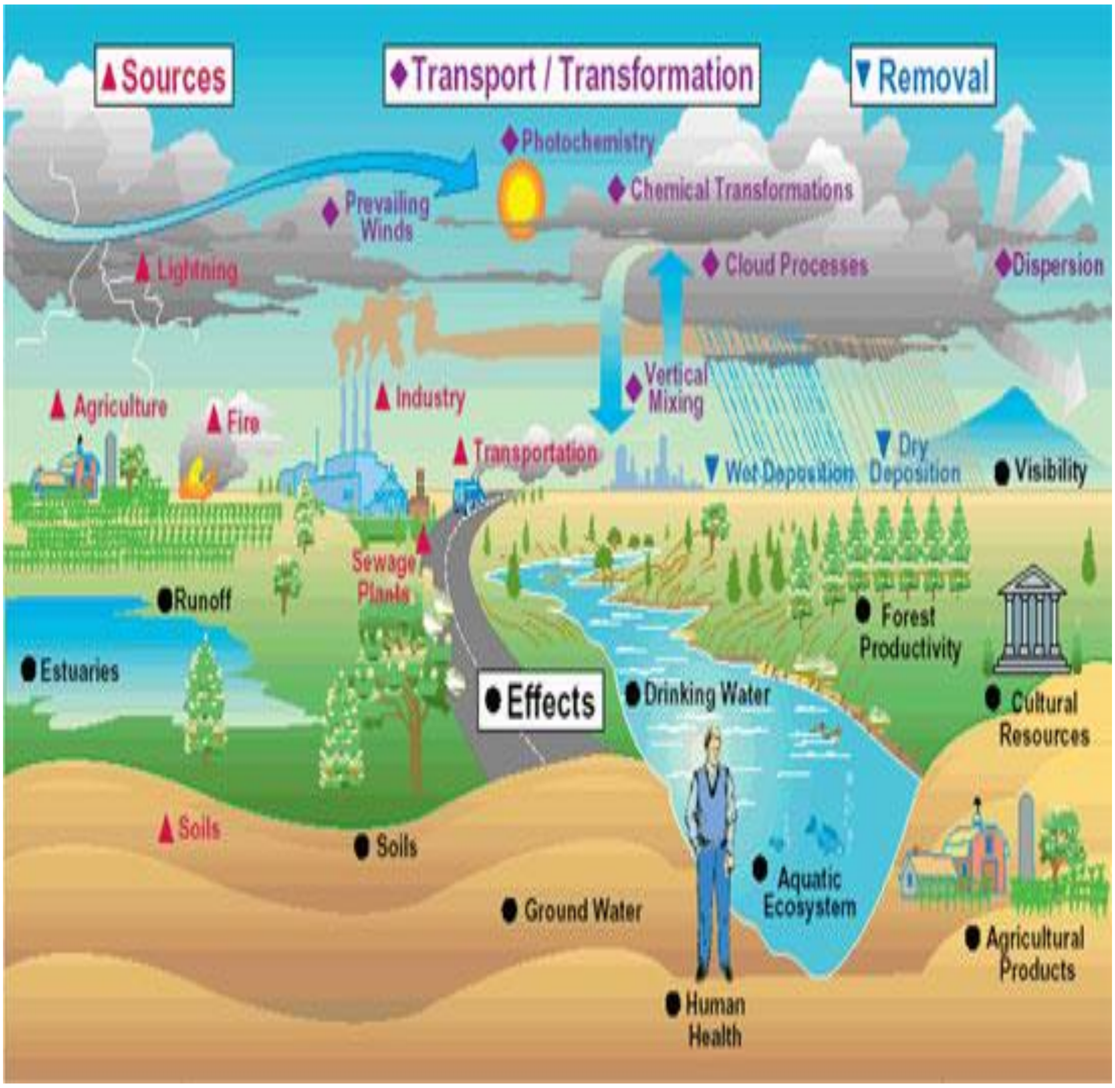
Concerning distribution, procedures are generally available for measuringpartitioning in aquatic systems, vapour-particulate distribution in the atmosphere, and binding to particles of various types in soils. Such information, together with information about relative binding strengths, allows us in many cases to make quantitative predictions about release rates and subsequent transport in aquatic systems and atmospheric environments. Biological involvement is also beginning to be described in quantitative terms, such as uptake from water by aquatic biota and uptake from soils by plants. Influence of biota on physical transport has also been studied.

Quantitative prediction of transport has advanced greatly in recent years, although some areas remain less well understood than others. Probably best understood are aquatic transport and surface runoff of pesticides and agricultural fertilizers. Short-range atmospheric transport has been well studied, while long-range transport is qualitatively understood but so far beyond the power of existing computer. Groundwater, that is, subsurface transport, will require much more study [1].

Transformation, for the present regarded as transformation to a chemicalform which is still of concern in terms of toxicity, has been widely studied andcontinues to be an active area of research, particularly for metals. Evensuch a familiar question as the methylation of mercury is not resolved; originally it was thought that biological transformation took place at a more-or-less constantrate and many subsequent studies have regarded this as axiomatic. It is now realized that various processes of demethylation as well as methylation are at work, and the net result is probably an equilibrium level of methyl versus inorganic forms. Similar analyses for other heavy metals and other elements are at a much less advanced stage [2].

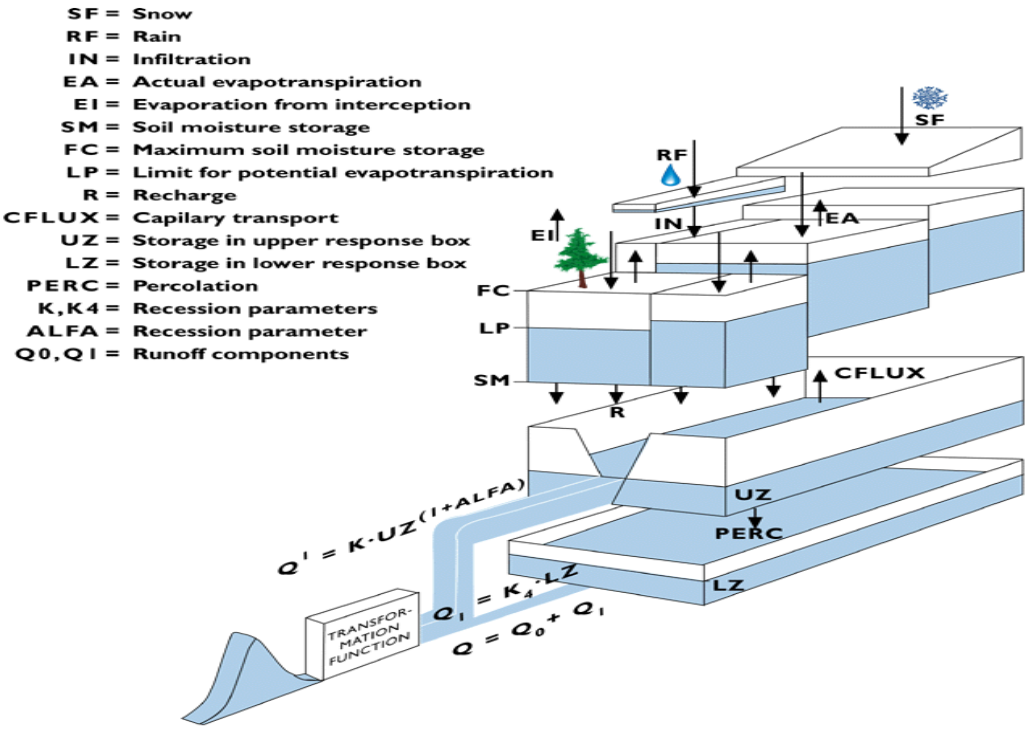
Analytic procedures for the various organometallic compounds are not trivial, and transformation from one to another may be spontaneous and fairly rapid. Few standardized procedures are available at present. Knowledge of the relative amounts of each species present is critical because of their great differences in toxicity. Much work remains to be done in this area [3].

Figure.4.5. Pollution dynamics in ecosystem [13].



Water quality modelling involves the prediction of water pollution using mathematical simulation techniques. A typical water quality model consists of a collection of formulations representing physical mechanisms that determine position and momentum of pollutants in a water body. Models are available for individual components of the hydrological system such as surface runoff; there also exist basin wide models addressing hydrologic transport and for ocean and estuarine applications. Often finite difference methods are used to analyse these phenomena, and, almost always, large complex computer models are required [7].

Figure.4.6. Hydrological model is the basis for water quality modelling [14].



Atmospheric dispersion modelling is the mathematical simulation of how air pollutants disperse in the ambient atmosphere. It is performed with computer programs that solve the mathematical equations and algorithms which simulate the pollutant dispersion. The dispersion models are used to estimate the downwind ambient concentration of air pollutants or toxins emitted from sources such as industrial plants, vehicular traffic or accidental chemical releases. They can also be used to predict future concentrations under specific scenarios (i.e. changes in emission sources). Therefore, they are the dominant type of model used in air quality policy making. They are most useful for pollutants that are dispersed over large distances and that may react in the atmosphere. For pollutants that have a very high spatio-temporal variability (i.e. have very steep distance to source decay such as black carbon) and for epidemiological studies statistical land-use regression models are also used.

Dispersion models are important to governmental agencies tasked with protecting and managing the ambient air quality. The models are typically employed to determine whether existing or proposed new industrial facilities are or will be in compliance with the National Ambient Air Quality Standards (NAAQS) in the United States and other nations. The models also serve to assist in the design of effective control strategies to reduce emissions of harmful air pollutants. During the late 1960s, the Air Pollution Control Office of the U.S. EPA initiated research projects that would lead to the development of models for the use by urban and transportation planners. A major and significant application of a roadway dispersion model that resulted from such research was applied to the Spadina Expressway of Canada in 1971.

Air dispersion models are also used by public safety responders and emergency management personnel for emergency planning of accidental chemical releases. Models are used to determine the consequences of accidental releases of hazardous or toxic materials, Accidental releases may result in fires, spills or explosions that involve hazardous materials, such as chemicals or radionuclides. The results of dispersion modelling, using worst case accidental release source terms and meteorological conditions, can provide an estimate of location impacted areas, ambient concentrations, and be used to determine protective actions appropriate in the event a release occurs. Appropriate protective actions may include evacuation or shelter in place for persons in the downwind direction. At industrial facilities, this type of consequence assessment or emergency planning is required under the Clean Air Act (United States) (CAA) codified in Part 68 of Title 40 of the Code of Federal Regulations.

The dispersion models vary depending on the mathematics used to develop the model, but all require the input of data that may include:

Meteorological conditions such as wind speed and direction, the amount of atmospheric turbulence (as characterized by what is called the "stability class"), the ambient air temperature, the height to the bottom of any inversion aloft that may be present, cloud cover and solar radiation.

Source term (the concentration or quantity of toxins in emission or accidental release source terms) and temperature of the material. Emissions or release parameters such as source location and height, type of source (i.e., fire, pool or vent stack) and exit velocity, exit temperature and mass flow rate or release rate.

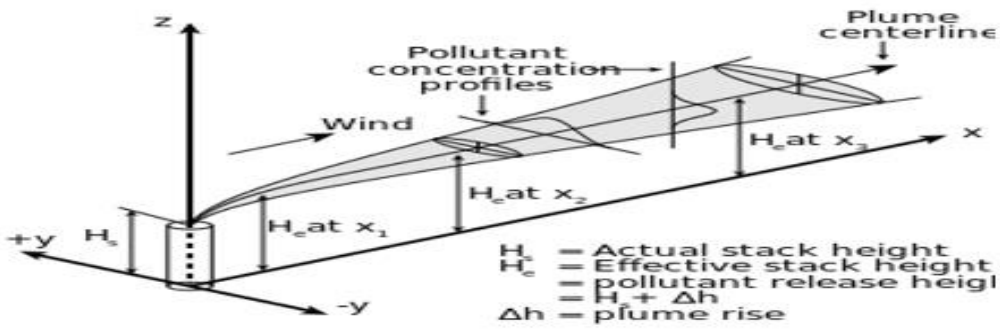
Terrain elevations at the source location and at the receptor location(s), such as nearby homes, schools, businesses and hospitals.

The location, height and width of any obstructions (such as buildings or other structures) in the path of the emitted gaseous plume, surface roughness or the use of a more generic parameter "rural" or "city" terrain.

Many of the modern, advanced dispersion modelling programs include a pre-processor module for the input of meteorological and other data, and many also include a post-processor module for graphing the output data and/or plotting the area impacted by the air pollutants on maps. The plots of areas impacted may also include isopleths showing areas of minimal to high concentrations that define areas of the highest health risk. The isopleths plots are useful in determining protective actions for the public and responders.

The atmospheric dispersion models are also known as atmospheric diffusion models, air dispersion models, air quality models, and air pollution dispersion models [4-5-6].

Figure. 4.7. Gaussian air quality and pollution transport model.



$$c(x,y,z) = \frac{q}{2\pi \bar{u} \sigma_y \sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2}\right) \pm \exp\left(-\frac{(z+h)^2}{2\sigma_z^2}\right)\right]$$

Groundwater models are computer models of groundwater flow systems, and are used by hydrogeologists. Groundwater models are used to simulate and predict aquifer conditions. An unambiguous definition of "groundwater model" is difficult to give, but there are many common characteristics.

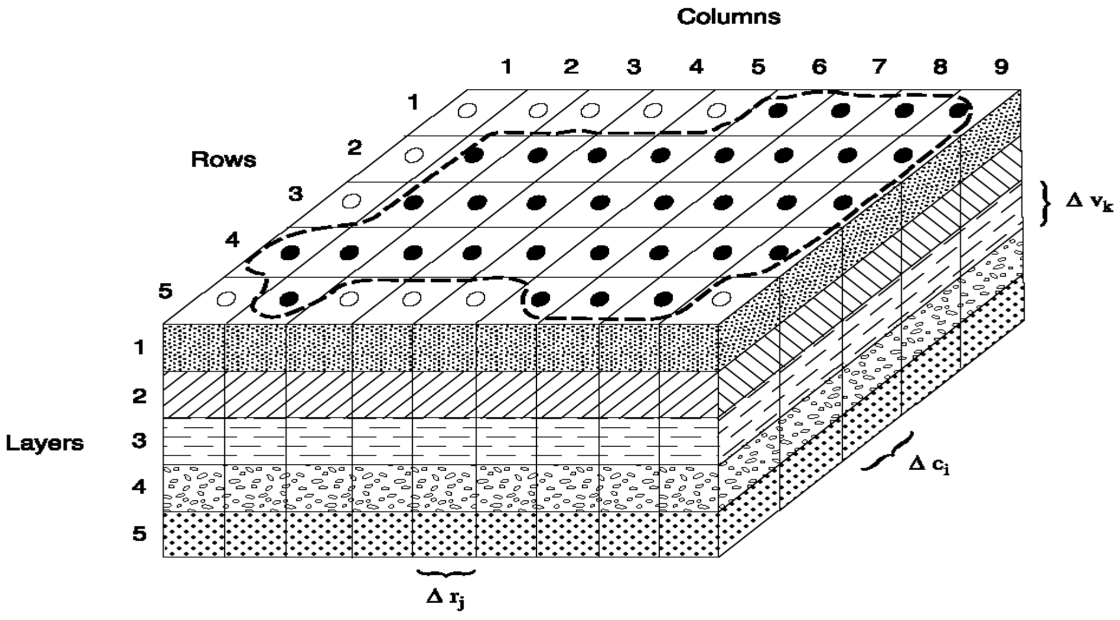
A groundwater model may be a scale model or an electric model of a groundwater situation or aquifer. Groundwater models are used to represent the natural groundwater flow in the environment. Some groundwater models include (chemical) quality aspects of the groundwater. Such groundwater models try to predict the fate and movement of the chemical in natural, urban or hypothetical scenario.

Groundwater models may be used to predict the effects of hydrological changes (like groundwater abstraction or irrigation developments) on the behavior of the aquifer and are often named groundwater simulation models. Also nowadays the groundwater models are used in various water management plans for urban areas.

As the computations in mathematical groundwater models are based on groundwater flow equations, which are differential equations that can often be solved only by approximate methods using a numerical analysis, these models are also called mathematical, numerical, or computational groundwater models.

The mathematical or the numerical models are usually based on the real physics the groundwater flow follows. These mathematical equations are solved using numerical codes such as MODFLOW, ParFlow, HydroGeoSphere, OpenGeoSys etc. Various types of numerical solutions like the finite difference method and the finite element method are applied [9].

Figure.4.8. Ground water model (https://en.wikipedia.org/wiki/Groundwater_model).



4.2.7. Fate in the environment [1-2-3]

As used here, 'fate' refers to the ultimate disposition of the chemical in theecosystem, either by chemical or biological transformation to a new form whichis nontoxic (degradation) or, in the case of an ultimately persistent substancesuch as heavy metal, by sequestering in a marine sediment or other locationwhich is expected to remain undisturbed.

For substances which are effectively degraded, whether by hydrolysis, photolysis, microbial degradation or whatever, it would seem necessary to collectand tabulate parameters which could serve as predictors for the rates at whichdegradation would occur. This has been attempted in some large studiesbut work is impeded simply because most such parameter values do not exist in the literature. On the other hand, work is progressing in establishing standard protocols for their determination.

Releases into the environment of persistent chemicals lead to an exposure levelwhich ultimately depends on the length of time the chemical remains incirculation, and how many times it is recirculated in some sense, before ultimate removal. This question must be carefully analysed through a study of globaldynamics, as has been done in relatively few cases. A particular question which needs to be addressed more often for metals is what fraction of the general global circulation is to be attributed to man's activities, an examination which can be made either on theoretical grounds or experimentally. Results are not always in agreement; for mercury, for example, estimates of the fractional global circulation which originates with man range from 5 per cent to as much as 30 per cent.

4.2.8. Effect on the physical environment [3]

There is some literature on the general ways in which pollution can affect thephysical and chemical nature of the environment, but the best approach is probably through examples of the various possibilities.

The generation of heat, usually by use of river or lake water for cooling of apower generating plant, has been well studied in terms of the total amount of heatgenerated and the temperature rise in the environment that will result. However, the general and ultimate alterations that will be produced in the environment are hard to predict. Certainly, it is not clear that all effects are necessarily adverse; increase in temperature may lead to much higher growth rates of commercially important species, for example.

The general attitude is that any change from the original state is to be avoided, although the possibility of making a change to a somehow more desirable ecosystem does come through in thoughtful reviews.

Changes in the acidity of a system, particularly an aquatic system, resulting rom acid rainfall are generally understood and the ecological consequences havebeen described at length. Similarly, changes in the acidity of terrestrial ecosystems have been widely studied in terms of the effect of a given change in pH, although the extent to which such a change is due to rainfall as opposed to natural acidification processes in the soil is not known. What is known, of course, is that pH changes can drastically affect the structure and function of the ecosystem, both directly and indirectly by, for example, increasing the concentration of heavy metals in the water through increased leaching from sediments. This general theme is further developed in the following chapters and in the case studies.

There are, of course, many other categories of physical and chemical effects, but detailed examination would be beyond the scope of this work. The reader is referred to the case studies for specific situations in which major changes in the ecosystem have resulted from alterations in the physical environment.

4.2.9. Environmental toxicology [8]

Environmental toxicology, also known as entox, is a multidisciplinary field of science concerned with the study of the harmful effects of various chemical, biological and physical agents on living organisms. Ecotoxicology is a sub discipline of environmental toxicology concerned with studying the harmful effects of toxicants at the population and ecosystem levels.

Rachel Carson is considered the mother of environmental toxicology, as she made it a distinct field within toxicology in 1962 with the publication of her book Silent Spring, which covered the effects of uncontrolled pesticide use. Carson's book was extensively based on a series of reports made by Lucille Farrier Stickel on the ecological effects of the pesticide DDT.

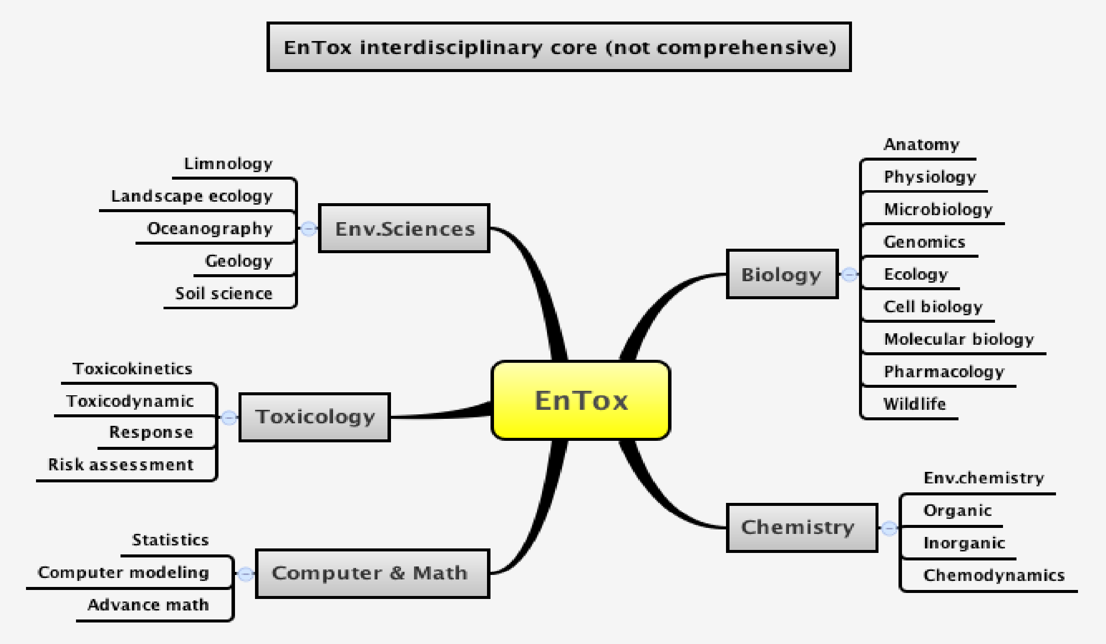
Organisms can be introduced to toxicants at various stages of their life cycle. The degree of toxicity can vary depending on where the organism is found within its food web. Bioaccumulation occurs when molecular compounds are stored in an organism's fatty tissues. Over time, this leads to the establishment of a trophic cascade and the bio magnification of specific toxicants. Biodegradation releases CO2 and water as by-products into the environment. This process is typically limited in areas affected by environmental toxicants.

Harmful effects of chemical and biological agents can include toxicants from pollutants, insecticides, pesticides, and fertilizers, all of which can impact an organism and its community through shifts in species diversity and abundance. Resulting changes in population dynamics impact the ecosystem by altering its productivity and stability.

Legislation has been implemented since the early 1970s to ensure that harmful effects of environmental toxicants are minimized for all species. Unfortunately, we are facing the risk of entering in a "dark age" due to longstanding limitations in the implementation of the simple conceptual modes

There are many sources of environmental toxicity that can lead to the presence of toxicants in our food, water and air. These sources include organic and inorganic pollutants, pesticides and biological agents, all of which can have harmful effects on living organisms. There can be so called point sources of pollution, for instance the drains from a specific factory but also non-point sources (diffuse sources) like the rubber from car tires that contain numerous chemicals and heavy metals that are spread in the environment.

Figure.4.9. The core of toxicology (https://en.wikipedia.org/wiki/Environmental_toxicology).



4.2.10. PCBs

Polychlorinated biphenyls (PCBs) are organic pollutants that are still present in our environment today, despite being banned in many countries, including the United States and Canada. Due to the persistent nature of PCBs in aquatic ecosystems, many aquatic species contain high levels of this chemical. For example, wild salmon (Salmo Salar) in the Baltic Sea have been shown to have significantly higher PCB levels than farmed salmon as the wild fish live in a heavily contaminated environment.

4.2.10.1. Heavy metals

Heavy metals found in food sources, such as fish can also have harmful effects. These metals can include mercury, lead and cadmium. It has been shown that fish (i.e. rainbow trout) are exposed to higher cadmium levels and grow at a slower rate than fish exposed to lower levels or none. Moreover, cadmium can potentially alter the productivity and mating behaviours of these fish. Heavy metals can not only affect behaviours, but also the genetic makeup in aquatic organisms. In Canada, a study examined genetic diversity in wild yellow perch along various heavy metal concentration gradients in lakes polluted by mining operations. Researchers wanted to determine as to what effect metal contamination had on evolutionary responses among populations of yellow perch. Along the gradient, genetic diversity over all loci was negatively correlated with liver cadmium contamination. Additionally, there was a negative correlation observed between copper contamination and genetic diversity. Some aquatic species have evolved heavy metal tolerances. In response to high heavy metal concentrations a Dipteran species, Chironomus riparius, of the midge family, Chironomidae, has evolved to become tolerant to Cadmium toxicity in aquatic environments. Altered life histories, increased Cd excretion, and sustained growth under Cd exposure is evidence that shows that Chironomus riparius exhibits genetically based heavy metal tolerance.

4.2.10.2. Pesticides

Pesticides are a major source of environmental toxicity. These chemically synthesized agents have been known to persist in the environment long after their administration. The poor biodegradability of pesticides can result in bioaccumulation of chemicals in various organisms along with bio magnification within a food web. Pesticides can be categorized according to the pests they target. Insecticides are used to eliminate agricultural pests that attack various fruits and crops. Herbicides target herbal pests such as weeds and other unwanted plants that reduce crop production.

4.2.11. DDT

Dichlorodiphenyltrichloroethane (DDT) is an organ chlorine insecticide that has been banned due to its adverse effects on both humans and wildlife. DDT's insecticidal properties were first discovered in 1939. Following this discovery, DDT was widely used by farmers in order to kill agricultural pests such as the potato beetle, coddling moth and corn earworm. In 1962, the harmful effects of the widespread and uncontrolled use of DDT were detailed by Rachel Carson in her book The Silent Spring. Such large quantities of DDT and its metabolite Dichlorodiphenyldichloroethylene (DDE) that were released into the environment were toxic to both animals and humans.

DDT is not easily biodegradable and thus the chemical accumulates in soil and sediment runoff. Water systems become polluted and marine life such as fish and shellfish accumulate DDT in their tissues. Furthermore, this effect is amplified when animals who consume the fish also consume the chemical, demonstrating bio magnification within the food web. The process of bio magnification has detrimental effects on various bird species because DDT and DDE accumulate in their tissues inducing egg-shell thinning. Rapid declines in bird populations have been seen in Europe and North America as a result.

Humans who consume animals or plants that are contaminated with DDT experience adverse health effects. Various studies have shown that DDT has damaging effects on the liver, nervous system and reproductive system of humans.

By 1972, the United States Environmental Protection Agency (EPA) banned the use of DDT in the United States. Despite the regulation of this pesticide in North America, it is still used in certain areas of the world. Traces of this chemical have been found in noticeable amounts in a tributary of the Yangtze River in China, suggesting the pesticide is still in use in this region.

4.2.11.1. Sulfuryl fluoride

Sulfuryl fluoride is an insecticide that is broken down into fluoride and sulphate when released into the environment. Fluoride has been known to negatively affect aquatic wildlife. Elevated levels of fluoride have been proven to impair the feeding efficiency and growth of the common carp (Cyprinus carpio). Exposure to fluoride alters ion balance, total protein and lipid levels within these fish, which changes their body composition and disrupts various biochemical processes.

4.2.13. Pros. and Cons.

Why we should pursue regulations and protections?

There is an economic value to protect the environment.

When we clear the environment for development, there is a loss of biodiversity. If, for instance, the logging industry cuts down an old-growth forest, and plants trees after they are done, the forest can take thousands of years to return to its original state.

Regulations like a carbon-tax can protect the environment by limiting greenhouse gases.

The natural beauty would be preserved.

The resources that we do have are non-renewable. So destroy the environment for resources that would only last a small amount of time?

We do not do enough as it is to preserve the environment.

Small business would be hurt dramatically. The incentive to go into small business and to be an entrepreneur is to make money. Additional environmental regulations would reduce this cash incentive even more. Remember, America's economic system was founded on rags to riches.

There is a possibility that regulations would have serious repercussions on the economy. That scenario includes heightened unemployment, and even less American manufacturing.

Places like the National Petroleum Reserve are beautiful, but how many people actually witness its beauty?

Technology is already processing towards reducing our carbon emissions.

Exercises Questions for Chapter 4 (Health)

1. In any activity where it is used or where workers may be exposed to dangerous chemical agents, there may be a risk to health.

a) True

b) False

2. What are the routes of entry into the human body from chemical.

a) inhalation, skin (or eye) absorption

b) inhalation, skin (or eye) absorption, ingestion, and injection.

c) inhalation, Ingestion and injection

d) Ingestion and injection

3. Occupational exposure limit values (OELs) are set to prevent occupational diseases or other adverse effects in workers exposed to hazardous chemicals in the workplace.

a) True

b) False

4. The identification of chemicals in terms of environmental contamination that should be considered.

a) Quantity of product used

b) Hazards (in terms of their toxicity)

c) Exposure time (dose)

d) All previous

5. Measures for the prevention and control of chemical health risks include:

a) Engineering Controls

b) Administrative practices

c) Personal protective equipment

d) All previous

6. Certain groups of workers may be at increased risk when working with dangerous substances. This may be due to several reasons:

a) Poor working conditions and Inexperience (coupled with inadequate supervision)

b) Increased susceptibility to the effects of chemicals and Communication difficulties

c) Lack of training or experience and lack of access to preventive services

d) All previous

7. Where to find toxicity information:

a) Only at the manufacturer

b) Safety Data Sheets

c) Only in packaging

d) None of the previous

8. How many headings contain the Safety Data Sheets (SDS):

a) 10

b) 20

c) 16

d) 11

9. What information needs to be provided on a Safety Data Sheets (SDS)?

a) Identification of the substance/mixture and of the company/undertaking; Hazards identification; Composition/information on ingredients; First-aid measures;

b) Fire-fighting measures; Accidental release measures; Handling and storage; Exposure controls/personal protection;

c) Physical and chemical properties; Stability and reactivity; Toxicological information; Ecological information; Disposal considerations; Transport information; Regulatory information; Other information;

d) All previous

10. The safety data sheet can´t be easily accessed by your employees and by emergency services.

a) True

b) False

11. When working with chemicals it is necessary to follow the rules of personal hygiene including:

a) Always wash your hands after handling chemicals

b) Not eat, drink or smoke in handling or near the storage site

c) Separate work clothes from other clothes

d) All previous

12. Safety and hygiene in the workplace should be a priority when using dangerous substances:

a) The use of Personal Protective Equipment when working with hazardous substances is always necessary

b) You do not need any special training to work with hazardous substances

c) Warning signs and labelling of products are only the responsibility of the manufacturer and not the user

d) Isn´t necessary that the safety data sheets on all hazardous products are available

13. The Personal Protective Equipment we can consider that these are:

a) The first choice in relation to protection measures

b) Should be used by the risk, when other measures are Insufficiently effective

c) Its correct usage results in the total elimination of the risks to which the people is exposed

d) Non previous

14. The Human health effects caused by exposure to toxic substances fall into two categories: short-term and long-term effects. Short-term effects (or acute

effects) have a relatively quick onset (usually minutes to days) after brief exposures to relatively high concentrations of material (acute exposures).

a) True

b) False

15. Which of these groups is usually designated as one of the most sensitive sub-populations for exposures to toxic substances:

a) Adult women

b) Adult men

c) Infants

d) Adolescents

Answers for Chapter 4 (Health)

1. True
2. B
3. True
4. D
5. D
6. D
7. B
8. C
9. D
10. False
11. D
12. A
13. C
14. True
15. C

Questions for Chapter 4 (Environment)

1. Can be said that environmental aspect is reason and environmental impact is consequence

a) yes

b) no

2. Environmental indicator is wider concept than environmental index

a) yes

b) no

3. Main environmental aspects of iron and steel industry are dealing with material and energy questions

a) yes

b) no

4. There is no waste water emissions from coke oven plant

a) yes

b) no

5. The major greenhouse gases are CO2 and CH4

a) yes

b) no

6. The IPPC directive includes not a permission procedure

a) yes

b) no

7. By mathematical modelling it is possible to describe, how chemicals distribute or change in environment

a) yes

b) no

8. Basis of water quality modelling is hydrological system

a) yes

b) no

9. Air dispersion models are used for emergency planning

a) yes

b) no

10. Groundwater flow can be described by differential equations and solved by numerical methods

a) yes

b) no

11. Non-point pollution sources are not significant for environment

a) yes

b) no

12. Heavy metals cannot affect genetic changes in aquatic organisms

a) yes

b) no

13. Acid waste water and water

a) accumulate on fish bodies

b) increases erosion

c) can clarify recipient water

d) causes oxygen depletion

14. Modelling of environmental impact can be based on

a) chemical characteristics

b) measurements

c) formulas of physical phenomena

d) public questionnaires

15. Chemicals in soil, groundwater and surface water; what is correct:

a) Darcy’s law describes chemical reactions in soil

b) Nutrients cause secondary oxygen demand in lakes

c) Chemical behaviour in soil depends also of grain size of soil particles

d) Oil does not move with ground water

16. Point “X” for correct terms

a) Emission = Cd released to soil

b) Environmental aspect = acidulation

c) CO2 (kg) emission = environmental indicatory

d) A collection of operations = system

17. What is correct:

a) Number of chemicals is reducing

b) Sinter plant forms high dust emissions

c) Heat recovery has no potential opportunity in sinter plant

d) iron-rich solids can be recycled to sinter plants

18. Coke oven plants

a) No VOC emissions can happen

b) Waste water is a relevant emission

c) Energy saving is essential

d) Energy saving minimize air emissions

19. What is correct:

a) Blast furnace is very energy efficient process

b) Solid residues are relevant environmental aspect of oxygen steelmaking

c) Organic compound are released from electric arc furnace

d) Filter slag is one problem is electric arc furnace

20. What is correct:

a) Nutrients cause acidification

b) Metal emissions cause eutrophication

c) SO_2 and NOx are acidifying cases

d) CO_2 is most famous greenhouse gas

21. Classification of environmental impacts:

a) All acids have same force of acidification

b) Eutrophication and oxygen demand are linking together

c) Global warming is caused by greenhouse gases

d) CO_2 is stronger greenhouse gas than CH_4

22. Quantitative transport of chemicals in ecosystem:

a) Aquatic transport is best known

b) Chemicals in water are stable

c) Water quality models describes physical phenomena

d) Gaussian air model is basing on normal distributions

23. Ground water models:

a) Includes only water hydraulic

b) Finite different and finite element methods are applied

c) are formed as 3D matrix

d) Chemical transport can be calculated using groundwater models

24. Environmental toxicity:

a) Consequences of toxic materials depends on food web of ecosystem

b) Pesticides are not toxic

c) Organic pollutants never are toxic

d) There is a positive correlation between copper and genetic diversity

Answers for Chapter 4 (Environment)

1. Yes
2. Yes
3. Yes
4. Yes
5. Yes
6. Yes
7. Yes
8. Yes
9. Yes
10. Yes
11. No
12. No
13. B and C
14. A, B and C
15. B and C
16. A, C and D
17. B and D
18. B, C and D
19. B
20. C and D
21. B and C
22. A, C and D
23. B, C and D
24. A

CHAPTER 5

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5. CHEMICAL ACCIDENTS

5. 1. Response

5.1.1. General

5.1.1.1. Course objectives/identification

The objectives of the course are as follows:

- to learn to know principles of tactics and methods when responding to a chemical accident
- to learn to know what can be done by emergency services in chemical response
- to learn to know where response instructions can be found
- to learn to know what kind of equipment and protecting devices are needed in response work

5.1.1.2. Course outcomes

As the outcomes of this course could be mentioned, among other things, the following:

- to know how and where response instructions can be found for different hazardous materials
- to know how hazard identification system can be utilized for finding a suitable response tactic and methods
- to get an idea what measures are needed to prepare for a special chemical accident (personal protecting equipment, chemical suits etc.)
- to know how response methods could be trained in advanced

5.1.1.3. Course terminology

- Area of direct hazard
- Chemical diving
- Isolation area
- A routine accident situation
- A demanding accident situation
- Starting point
- Rinsing area

- Decontamination area
- First aid post
- Service post
- A pair of chemical divers
- Stand-by pair
- Chemical diving unit
- Chemical protective clothing (chemical protective suit).
- Outer suit for cold protection
- Splash suit
- Breathing apparatus
- Filtering device
- Protection jet

5.1.1.3. Classification

Classification is a part of chemical accidents.

5.1.1.4. Operation (how it is used)

This training module includes theory and description of typical response methods and equipment both the personal protecting devices and suits. It includes also training instructions for different accident situations. After studying the text section there is a training section about questions to be answered (It was given at the end of this chapter).

5.1.1.5. Pros. and Cons.

A. Pros.

- Even there are thousands of different chemicals, in reality, there are only few decades of chemicals that typically cause chemical accidents in larger scale (especially in transportations of hazardous materials).
- Tactical guides and response methods can be chosen according to ADR groups or subclasses, and they are not so many.

B. Cons.

The response methods described here demand special expertise and are mainly done by professionals.

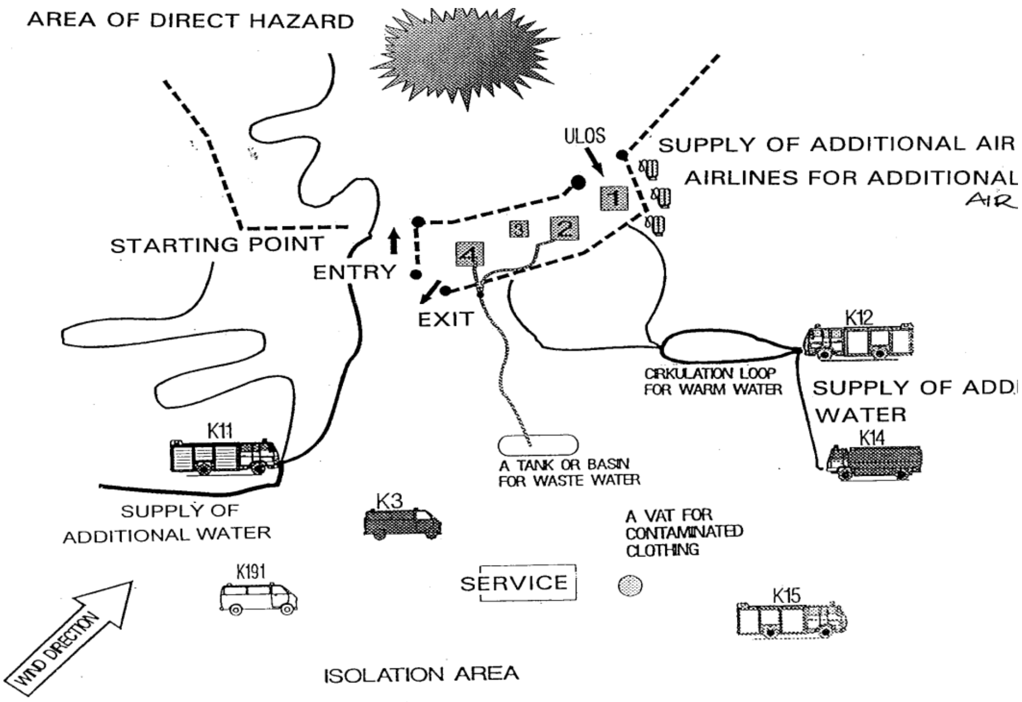
5.1.2. Definition of chemical response [1]

In chemical accident situations response actions are mainly taken by professional emergency services or fire brigades that are trained to do this kind of dangerous work. The following terms are related to response work done by professionals (emergency services).

- Area of direct hazard, the area or enclosed space to which a chemical with a health, environmental or fire hazard has spread, or where the oxygen concentration of air has decreased. Also an area or enclosed space which is suspected to be, or may become hazardous.
- Chemical diving, the going to the area of direct hazard wearing respiratory protection and other necessary personal protection, to perform a reconnaissance, rescue, mitigation, or similar task.
- Isolation area, the area surrounding the area of direct hazard, from which bystanders are removed, and which is roped off to provide working space for the fire brigade.
- A routine accident situation an accident situation in which the chemical diving task can be performed by one chemical diving team, there are no particular hazards or poor visibility, and the contaminated personal protective equipment can be rinsed in the rinsing area.
- A demanding accident situation an accident situation in which the chemical diving task cannot be performed by one chemical diving team, or there are particular or insufficiently known hazards, or poor visibility, or the contaminated personal protective equipment must be washed in the decontamination area.
- Starting point, a point where the chemical divers enter the area of direct hazard and where they return, passing through a rinsing or decontamination area.
- Rinsing area, a rinsing area must always be set up before the start of chemical diving. An area where the chemical divers returning from the area of direct hazard, the victims rescued and material used are rinsed. The rinsing area is set up close to the starting point, and at the border between the area of direct hazard and the isolation area
- Decontamination area, if a toxic and insoluble chemical has been spilled, or there are several chemical divers to be rinsed, the chemical divers returning from the area of direct hazard, and the material used by them are washed in the decontamination area and the washing water is contained (Figure 5.1).

- First aid post, a post where the victims and injured chemical divers are given first aid, after they have been rinsed or decontaminated. The first aid post is set up in the isolation area.
- Service post, a helper sets up a service post in the isolation area.
- A pair of chemical divers, two chemical divers: the first and the second chemical diver.
- Stand-by pair If necessary, the officer in charge assigns a stand-by pair, maintaining eye contact and communication with, and securing the return passage of the chemical diving team at work.
- Chemical diving unit, a rescue unit with a target strength of 1+5 and equipped with, at least, 3 sets of chemical protective clothing and 3 splash suits, and other equipment needed for chemical diving.
- Chemical protective clothing (chemical protective suit). A protective suit worn on a fire suit or other intermediate wear which, together with a breathing apparatus, provides the diver with a gas and liquid tight sealing from certain chemicals with a health hazard.
- Outer suit for cold protection, a protective suit worn outside chemical protective clothing to protect the latter from cold
- Splash suit, a protective suit worn on a fire suit or other intermediate wear, and which covers most of the body and protects it from splashes and dust.
- Breathing apparatus, a self-contained respiratory protective device with a supply of breathing air in cylinders.
- Filtering device, a respiratory protective device in which the ambient air passes through a filter.
- Protection jet, a spray jet used for rinsing the chemical divers, and the victims rescued from the direct hazard area, if necessary.

Figure.5.1. Decontamination area [1].



Photoghraph.5.1. Decontamination of chemical divers.

5.1.3. Choosing a tactic in chemical response

5.1.3.1. Tokeva instructions [1]

Response measures have a certain order of urgency and their feasibility depends on the resources available to the officer in charge. The experience from response to chemical accidents has proved that it is worthwhile to perform the measures in certain order.

General Response Tactics can be presented as follows:

1. Start reconnoitring and approach the accident site from an upwind direction.
2. Use personal protective equipment.
3. Rescue the victims.
4. Reconnoitre the leak and specify the hazard area. Organize the rinsing area.
5. Isolate the hazard area from bystanders and traffic.
6. How does the situation develop? Ask expert advice.
7. Prevent a fire or extinguish it.
8. Contain the spill.
9. Close or plug the leak.
10. Make the spillage harmless.
11. Report the environmental damage to authorities.
12. Stop the rescue activities.
13. Remove the restrictions.
14. Decontaminate clothing and equipment.

The starting point for the General Response Tactics has been a sudden accident: leak, spill or fire. There is no response plan for the accident site and the accident puts persons, property and/or the environment at risk.

Also members of the emergency team are subjected to health hazards. They have to use personal protective equipment and, possibly, to mitigate the risk of fire, explosion or tank rupture. Often, an adequate idea of the risks can be formed only after reconnoitring and expert evaluation of the situation has been made.

The risks have assumed to be large: a large leak or spill, chemical with health hazards, high ignition risk etc. Using the General Response Tactics, the officer in charge will be able to lead mitigation and rescue activities in such a situation in an effective and safe way.

An accident may often involve hazards not caused by the chemical itself, calling for prompt action. The hazards caused by the chemical may be slight in proportion to other hazards. It was possible to consider the other hazards in a limited way only when the response tactics and Guides were drafted. The following accident types, however, have been considered:

- There are injured and/or trapped persons to be rescued. The leaking chemical causes an ignition or explosion risk, is hazardous to health and/or is on fire.
- The leaking chemical or some other material is on fire and the thermal radiation or flame contact is heating leaking or intact containers.
- A toxic non-flammable chemical is evaporating or decomposing in a fire. A toxic aerosol is dispersing with the smoke.

Often the hazards caused by the chemicals are known or found to be small compared with the other hazards. The General Response Tactics and these instructions may be applied to such situations at discretion and if needed. On the other hand, they don't usually hamper the response.

At sites with a response plan, the action will follow the plan. The General Response Tactics and these instructions may be utilized to draft the response plan.

At industrial plants, in rail yards and chemicals harbours information on the type of accident and environmental conditions can often be got faster and more effectively than it was assumed when the instructions were drafted. The officer in charge may have e.g. wind gauges and fixed or portable gas detectors at his disposal. The accident consequences can be mitigated more effectively with fixed equipment such as water spray systems, water monitors, water or steam curtains etc.

Emergency services find the right tactical guide on the base of identification of hazardous material. F.ex. response guidebooks like Tokeva Instructions or Emergency Response guidebook gives a tactical guide, if chemical name or UN number is known. From Tokeva Instructions can be found a tactical guide also on the base of ADR group or hazard identification number. If hazardous chemicals are properly labelled, hazard identification number placard gives all information needed to find out a suitable tactical guide.

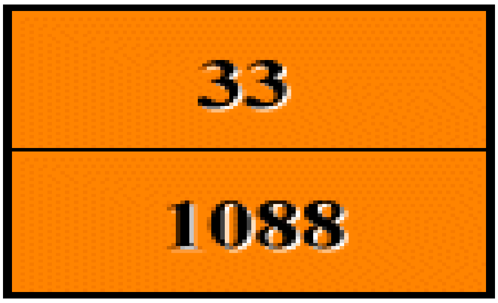
Figure.5.2. Hazard identification number placard.

According to *Tokeva* instructions tactical guide includes the following:

- **hazards** involved to the chemical
- **personal protective equipment**to be used
- **equipment**to be used
- **measures** to be done

A. EXAMPLE 1: UN number 1088 tells, that the chemical is acetal and hazardous identification number 33 warns about highly flammable liquid. On base on these information tactical guide can be found.

Figure. 5.3. Hazard identification number placard.



According to Tokeva Instruction there is tactical guides for both for non-ignited spill and for burning spill.

Guide T3b: Highly flammable liquids

A.1.Non-ignited spill

A.1.1. Hazards

- Ignition hazard of the spill, flashing vapours cause burns.

- Explosion hazard of vapours from a spill in a room or into the drain system. Dense vapours may flow into cellars and other low-lying spaces.
- Liquid spilled on ground or into a watercourse causes environmental damage.
- Breathing of vapours at high concentrations may cause dizziness, indisposition, headache and other such symptoms.

A.1.2. Personal protective equipment

- Fire suit.
- Plastic or rubber gloves.
- A non-burning splash suit.
- Breathing apparatus.

A.1.3. Equipment

- Spray jet to ventilate enclosed spaces and to dilute vapours.
- A (non-sparking) smoke ejector to ventilate enclosed spaces or the drain system.
- Eye wash bottle.
- Explosimeter (combustible gas indicator) to reconnoitre the hazard area.
- A gas detector with appropriate detector tubes.
- Warning signs and barricade tape to rope off a spill.
- Foam extinguishing equipment and some (for acetone alcohol resistant) foam concentrate.
- Shovels to dike the spill and to spread the sorbent.
- Pneumatic cushions to plug drain wells.
- Oil booms to contain the liquid leaking into a watercourse.
- Material for a pipe skimming dam: a flexible plastic tube, timber, plastic sheeting.
- (Non-sparking) hand tools to tighten a valve or flange.
- Wooden plugs and wedges to plug a leak.
- Putty to plug a leak.
- A neoprene rubber sheet and an aluminium sheet or a plywood board and lashing straps to seal a rupture.
- A pneumatic lifting or plugging cushion with lashing straps to seal a rupture.
- An explosion proof pump, hoses, earth conductors and ground rod.

- Folding basins, bags or containers to collect the spilled liquid.
- Peat or other sorbent.
- Vats (provided with lids) and plastic sheeting to collect used sorbent.

A.1.4. Measures

1. Start reconnoitring and approach the accident site from an upwind direction. Find out the nature, direct hazards and anticipated development of the accident. Try to identify the chemical involved. **Guide M1**.

2. Wear breathing apparatus and plastic or rubber gloves. Wear a splash suit near a leaking pressurized pipe etc. and during the pumping of liquid.

3. Rescue the victims if there is no ignition hazard. Remove the ignition hazard with foam, ventilation **Guide M7a** or a spray jet **Guide M8c**. Remove the contaminated clothing. Rinse the skin with lukewarm running water. Wash the skin with running water and liquid soap for 10 minutes. If the liquid has splashed into eyes rinse with running water for 10 minutes. Ask the victim to blink his or her eyes. **Guide M14**. If there is irritation after rinsing a medical examination is necessary.

4. A colourless liquid with a characteristic smell. Hazard area: the immediate surroundings of the pool. Reconnoitre the hazard area with an explosimeter. If necessary, a pair of chemical divers reconnoitre the location and size of the leak and the amount, appearance, behaviour and spreading of the leaking substance **Guide M4a.** Check enclosed spaces with an explosimeter **Guide M4a** and, if necessary, with a gas detector Guide M4c. Set up a rinsing area.

5. Remove bystanders from the hazard area and rope it off. Evacuate rooms where an ignition or health hazard is possible.

6. The ignition or explosion hazard may spread and the environmental damage may increase as more liquid is spilled. If liquid has flown into drain report the drain works. If liquid has spilled on ground or into a watercourse and expert advice is needed, contact the local environmental authority. To empty and lift a leaking road tanker, see **Guide M6a**.

7. Move containers threatened by fire or some other hazard or containers causing a hazard to a safe place. Ventilate enclosed spaces. Shut off ignition sources. Avoid all activities that may generate sparks such as the use of internal combustion engines and

radiophones. **Guide M7a**. Cover the spill with foam. Use alcohol resistant foam for acetone. **Guide M8d**.

8. Dike the spill with sand, earth, sorbent or with a fire hose filled with water. Contain the spill into a watercourse with oil booms or a pipe skimming dam. Prevent the spill from entering the drain system by plugging the gully holes. If liquid has flown into the drain prevent it from spreading in the drain system by plugging the drain wells on both sides of the spill site. **Guide M8b.** Ventilate a drain section by opening well covers. Rope off the immediate surroundings of the wells. You can make the ventilation more effective by blowing air into the drain with a non-sparking smoke ejector. Even an ordinary smoke ejector will do provided that there is no ignition risk close to the ejector. Ventilate those enclosed spaces where there are flammable vapours. **Guide M7a.**

9. Rotate the tank so that the leak comes above the liquid surface. Close the valve or tighten the valve or flange. Put a wet cloth between the nut and wrench to prevent sparking. Plug the leak with a wooden plug or wedge. Seal a rupture with a rubber sheet (propped with an aluminium sheet or a plywood board) or a pneumatic lifting or plugging cushion and lash it to the tank with straps. **Guide M9.**

10. Pump the liquid contained into a drain well or remaining in the damaged tank into a folding basin, vat or container with an explosion proof pump. Connect the tank to be emptied and the couplings of the suction and pressure hoses to the pump with earth conductors. Push the ground rod into moist soil and connect it to the pump with a similar conductor. **Guide M10a.** Absorb the remaining liquid into peat or other sorbent. Collect used sorbent into vats and cover them with lids or plastic sheeting. Label the vats with Mitigation Waste Labels. **Guide M10b.** If there is little risk of fire spread you may destroy the pool by burning (about a 5 mm thick liquid layer is consumed by fire in a minute).

11. If liquid has been spilled on ground or into a watercourse report to the regional environmental authority.

12. Stop the rescue activities.

13. Remove the restrictions.

14. Rinse the contaminated clothing and equipment with water. **Guide M14.**

A.2. Burning spill

A.2.1. Hazards

- The flames may spread the fire.
- A steel tank heated by the fire may be pressurized and rupture. The contents may burn as a fire ball. An aluminium tank melts, which prevents it from pressurizing. No fire ball is formed.
- The chemical mixed with used fire-fighting water may cause environmental damage.

A.2.2. Personal protective equipment

- Fire suit.
- Fire protective suit.
- Breathing apparatus indoors.

A.2.3. Equipment

- (Supported) water jets to cool the tank.
- Dry powder extinguishing equipment.
- Foam extinguishing equipment and some (for acetone alcohol resistant) foam concentrate.
- Spray jets.

A.2.4. Measures

1. Start reconnoitring and find out the nature, direct hazards and the spreading risk of the fire. **Guide M1.**

3. Rescue the victims if you can do it safely.

5. Remove bystanders from the hazard area and rope it off.

7. Move away the containers threatened by fire. If this is impossible, cool the heated part of the tank with fixed spray equipment or supported jets**. Guide M7b.** Extinguish the liquid fire with dry powder, water spray or (for acetone alcohol resistant) foam.

8. Dike the used fire-fighting water or collect it into a plugged drain well. **GuideM8b.**

12. Stop the rescue activities.

13. Remove the restrictions.

A.2.3. Emergency response guidebook 2012 (ERG2012) [2]

The ERG2012 is primarily a guide to aid first responders in quickly identifying the specific or generic hazards of the material(s) involved in the incident, and protecting themselves and the general public during the initial response phase of the incident.

Guide can be found easily on the base of UN number or chemical name.

B. EXAMPLE 2 In case of ammonia accident the following instruction is provided.

B.1. Health

- **TOXIC; may be fatal if inhaled, ingested or absorbed through skin.**
- Vapours are extremely irritating and corrosive.
- Contact with gas or liquefied gas may cause burns, severe injury and/or frostbite.
- Fire will produce irritating, corrosive and/or toxic gases.
- Runoff from fire control may cause pollution.

B.1.2. Fire or explosion

- Some may burn but none ignite readily.
- Vapours from liquefied gas are initially heavier than air and spread along ground.
- Some of these materials may react violently with water.
- Cylinders exposed to fire may vent and release toxic and/or corrosive gas through pressure relief devices.
- Containers may explode when heated.
- Ruptured cylinders may rocket.

B.1.3. Public safety

- **CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.**
- As an immediate precautionary measure, isolate spill or leak area for at least 100 meters (330 feet) in all directions.
- Keep unauthorized personnel away.

- Stay upwind.
- Many gases are heavier than air and will spread along ground and collect in low or confined areas (sewers, basements, tanks).
- Keep out of low areas.
- Ventilate closed spaces before entering.

B.1.4. Protective clothing

- Wear positive pressure self-contained breathing apparatus (SCBA).
- Wear chemical protective clothing that is specifically recommended by the manufacturer. It may provide little or no thermal protection.
- Structural firefighters' protective clothing provides limited protection in fire situations ONLY; it is not effective in spill situations where direct contact with the substance is possible.

B.1.5. Evacuation

B.1.5.1. Spill

- See Table 1 - Initial Isolation and Protective Action Distances for highlighted materials. For non-highlighted materials, increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".

B.1.5.2. Fire

- If tank, rail car or tank truck is involved in a fire, ISOLATE for 1600 meters (1 mile) in all directions; also, consider initial evacuation for 1600 meters (1 mile) in all directions.

B.1.6. Emergency response

B.1.6. 1. Fire

A. Small fire

- Dry chemical or CO2.

B. Large fire

- Water spray, fog or regular foam.
- Move containers from fire area if you can do it without risk.
- Do not get water inside containers.

- Damaged cylinders should be handled only by specialists.

C. Fire involving tanks

- Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
- Cool containers with flooding quantities of water until well after fire is out.
- Do not direct water at source of leak or safety devices; icing may occur.
- Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- ALWAYS stay away from tanks engulfed in fire.

B.1.7. Spill or leak

- Fully encapsulating, vapour protective clothing should be worn for spills and leaks with no fire.
- Do not touch or walk through spilled material.
- Stop leak if you can do it without risk.
- If possible, turn leaking containers so that gas escapes rather than liquid.
- Prevent entry into waterways, sewers, basements or confined areas.
- Do not direct water at spill or source of leak.
- Use water spray to reduce vapours or divert vapour cloud drift. Avoid allowing water runoff to contact spilled material.
- Isolate area until gas has dispersed.

B.1.8. First aid

- Move victim to fresh air.
- Call 911 or emergency medical service.
- Give artificial respiration if victim is not breathing.
- **Do not use mouth-to-mouth method if victim ingested or inhaled the substance; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.**
- Administer oxygen if breathing is difficult.
- Remove and isolate contaminated clothing and shoes.
- In case of contact with liquefied gas, thaw frosted parts with lukewarm water.

- In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes.
- **In case of contact with Hydrogen fluoride**, anhydrous (UN1052), flush skin and eyes with water for 5 minutes; then, for skin exposures rub on a calcium/gel combination; for eyes flush with a water/calcium solution for 15 minutes.
- Keep victim warm and quiet.
- Keep victim under observation.
- Effects of contact or inhalation may be delayed.
- Ensure that medical personnel are aware of the material(s) involved and take precautions to protect themselves.

Notice: ERG2012 is available on-line in Englishhttp://wwwapps.tc.gc.ca/saf-sec-sur/3/erg-gmu/erg/ergmenu.aspx **and Spanish**http://wwwapps.tc.gc.ca/saf-sec-sur/3/gre/gre/gremenu.aspx .

5.1.4. Typical chemical response methods [1]

M1: Reconnaissance of the accident site

M4a: Reconnaissance of the leak

M4b: Determination of ignition hazard

M4c: Determination of the hazard area of a toxic gas

M6a: Road tanker 3 ADR (inflammable liquids) discharge and lifting

M6b: Road tanker 2 ADR (non-flammable gases by freezing or pressure) discharge and lifting

M6c: Road tanker 2 ADR (pressurised liquefied inflammable gases) discharge and lifting

M6d: Road tanker 2 ADR (toxic gases liquefied under pressure) discharge and lifting

M7a: Removing ignition sources and ventilating

M7b: Cooling a tank

M8a: Covering a spray jet of a toxic liquid gas

M8b: Diking a spill, plugging a drain

M8c: Diluting and scrubbing a gas cloud

M8d: Controlling spill evaporation

M9: Closing or plugging a leak

M10a: Pumping

M10b: Use of sorbents

M10c: Neutralization

M14: Decontamination of clothing and equipment

C. EXAMPLE 3: M8a: Covering a spray jet of a toxic liquid gas

C.1. Situations

A toxic liquid gas is leaking from a defective valve, flange, pipe or tank.

The storage temperature of the liquid is at least 15°C above the boiling point. The liquid gas jet breaks into a spray which evaporates rapidly as air is entrained in the jet.

C.2. Equipment, personal protection, resources

- A plastic tarpaulin, 6 m x 10 m.
- A wide tube with about 40 cm diameter and 3 - 10 m long, e.g. a smoke ejector hose or a sack tube.
- Lashing straps and bands.
- Hand tools.
- To cover a tank wagon: A plastic tarpaulin with a 1,5 m long rope fixed at each corner and a side length of 21 m.3 sectional lifting bars, length 4 m. Scaling ladder.
- Spades.
- A folding basin.
- A team of chemical divers, to cover a tank wagon 2 pairs of chemical divers.
- Personal protective equipment of the chemical divers: a breathing apparatus with positive pressure, chemical protective clothing, an outer suit for cold protection (when required) and thermally insulating gloves.

C.3. Methods

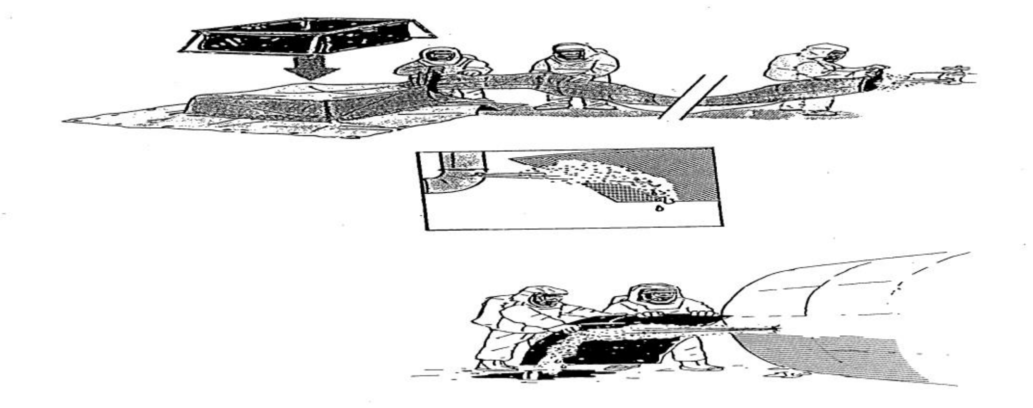
C.3.1. Preparation

- The mixing of air into a spray jet of liquid gas and the evaporation of the spray can be prevented by covering the jet with a plastic tarpaulin or directing it into a sack tube or any wide tube.
- The location of the leak (height above ground level and accessibility) determine the possibility to cover it. If the leak is located not higher than 1,5 m above ground firemen can cover it easily with a tarpaulin. A leak located higher (e.g. on the top of a tank wagon) is more difficult to cover.
- Depending on the location and size of the leak and the immediate surroundings either a tarpaulin or a wide tube is used to cover a leak.

C.3.2. The leak is close to ground level (Figure 5.4)

- Use the tarpaulin to erect a tent around the leak and secure the border e.g. by shovelling earth on it. In this way you will prevent the wind from blowing air under the tarpaulin. Direct the liquid collected by the tarpaulin into a folding basin or a pit (lined with another tarpaulin).
- Place a wide tube close to the leak so that the liquid spray jet is directed into the tube. Collect the liquid flowing from the tube into a folding basin or a pit (lined with another tarpaulin). Prevent air from flowing through the tube by closing the upper end behind the leak.

Figure.5.4. Covering the spray jet from a leak of toxic pressure liquefied gas when the leak is close to ground level [1].



C.3.3. The leak is on the top of a tank wagon (Figure 5.5)

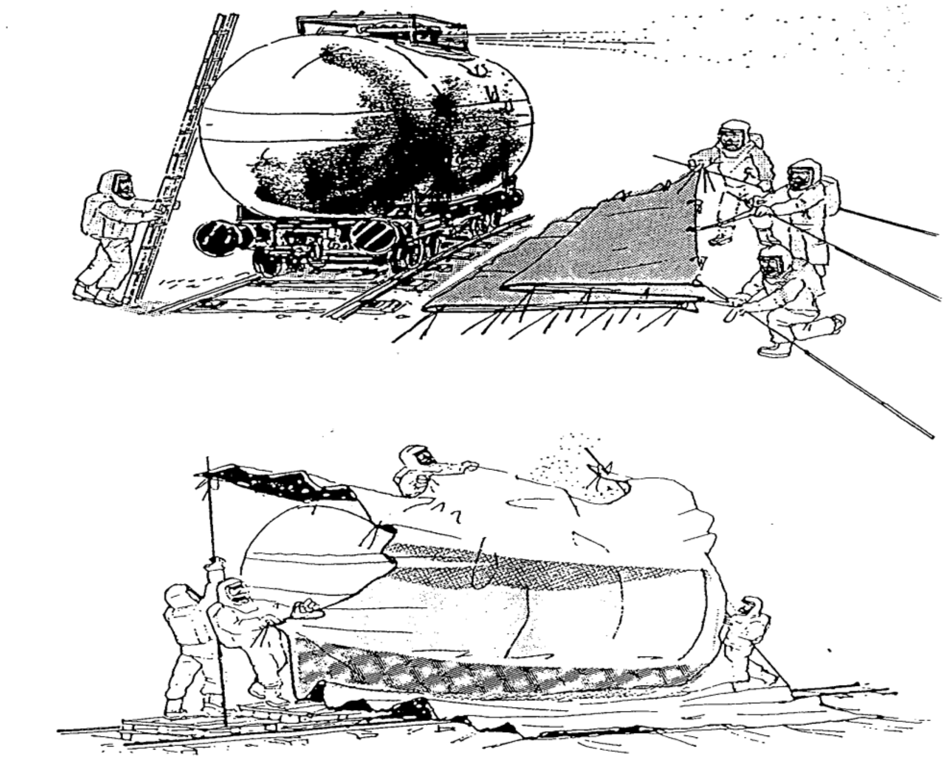
- Spread the tarpaulin out on ground beside the wagon. Chemical divers standing at both ends of the wagon lift the tarpaulin on the top of the wagon with lifting bars and pull it above the tank. A chemical diver standing on a scaling ladder (on the opposite site of the leak) assists.

- The tarpaulin is fastened in such a way that the liquid collected flows on the tarpaulin (but not on the tank wall) and into a folding basin or a pit (lined with another tarpaulin). Try to prevent the wind from blowing air under the tarpaulin.
- Place a wide tube close to the leak so that the liquid spray jet is directed into the tube. Direct the liquid flowing from the tube into a folding basin or a pit (lined with another tarpaulin). Prevent air from flowing through the tube by closing the upper end behind the leak.

C. 4. Training

- A spray jet of liquid gas can be simulated by steam or water jet.

Figure.5.5. Covering the spray jet from a leak of toxic pressure liquefied gas when the leak is on the top of a tank wagon [1].



5.1.5. Personal protectors

5.1.5.1. Breathing protection

A. Isolating

- breathing apparatus is a self-contained respiratory protective device or

- oxygen apparatus

Photograph. 5.2. Self-contained respiratory protective device.

B. Filtering

- total mask

- half mask

- oxygen content > 17 v-%
- substance is known
- proper filter
- still valid
- concentration of pollutant < 1 v-% = 10.000 ppm

Photoghraph.5.3. Filtering mask.

- dust mask

- Reliable, effective protection against fine particulates, good for protection against airborne infectious diseases.

Photograph.5.4. Dust mask.

5.1.5.2. Protective suits [2]

A. Protection level 1: Fire suit and breathing apparatus

- is used when responding to chemicals like argon, methane, naphthalene, potassium sulphide, zinc powder, sodium, ammonium nitrate

- can be used f. ex. when rescuing a victim

Photograph.5.5. Protection level 1 / fire suit and breathing apparatus [2].

B. Protection level 2: Splash suit and breathing apparatus

- splash suit must fulfil the requirements of standard prEN468

- is used when responding to chemicals like freon, asetaldehyde, carbon disulphide, white phophorus, gasoline, peroxyacetic, liquid and solid radioactive substances, zinc chloride.

Photograph.5.6. Protection level 2 / fire suit completed with splash suit and breathing apparatus [2].

C. Protection level 3: Chemical suit and breathing apparatus

- must be air-tight

- breathing apparatus can be under or above the chemical suit

- is used when responding to chemicals like nitrogen oxide, perchloric acid, aniline, phenol, chloroform, sulfuric acid (if breathing apparatus is above the chemical suit, the breathing apparatus has to be protected against sulfuric acid).

Photograph.5.7. Protection level 3 / chemical suit and breathing apparatus [2].

D. Protection level 4: Chemical suit completed with cold protective suit

D.1.Breathing apparatus

- must be air-tight

- breathing apparatus is under a cold protective suit

is used when responding to chemicals cold gases like ammonia, chlorine, hydrogen –chloride

Figure.5.8. Protection level 4 / chemical suit completed with cold protective suit and breathing apparatus [2].

5.1.5.3. Eyes protection

A. Safety goggles

- use safety goggles always when there is any chance for eyes to be exposed for dusts, vapours, splashes or light

- contact lenses should not be used

Figure.5.6. Safety goggles.

5.1.5.4. Hands protection

A. Protective gloves

- there are many materials in protective gloves

- natural rubber, PVC, nitrile, neoprene

- chemical resistance of material should be checked

Figure.5.7. Protective gloves.

5.1.5.5. Chemical resistance of materials

A. Laminate film (carbon fibre), f.ex. Barrigade ja Responder

\+ best chemical resistance

+suitable to most typical chemicals

- clumsy to handle

- mechanical strength not good

B. Nitrile

\+ suitablefor acids, bases, oils and greases

- f.eg. HCl, NaOH, acetic acid, gasoline, toluene

- not suitable for solvents containing ketones, oxidising acids and organic compounds containing nitrogen

- f.eg. acetone, strong H_2SO_4 and HNO_3, nitrobenzene

C. Neoprene

\+ multi-purpose chemical resistance

\+ very good for acids and aliphatic solvents

- HCl, H2SO4, methyl alcohol, acetone

- not suitable for chlorinated and aromatic solvents

- f.ex. benzene, chloroform, gasoline, toluene

D. Polyvinyl alcohol (PVA)

+ suitable for chlorinated and aromatic solvents

- chloroform, gasoline, toluene, xylene

\- not suitable for ketones, alcohols, acids, bases

- acetone, methyl alcohol, ethyl alcohol, HCl, NaOH

E. Polyvinyl chloride (PVC)

+ suitable for acids and bases

- HCl, HNO3, H2SO4, NaOH, NH4OH

\- not suitable for solvents containing ketones and aromatic solvents

- acetone, gasoline, benzene, toluene

F. Natural rubber

+ suitable for alcohols, ketones and weak acids

\- not suitable for aromatics, strong oxidizing acids and halogenated solvents

- gasoline, benzene, toluene, H2SO4, HNO3, chloroform

G. Polyamid (PA)

+ stands, oils, fats, vax, diluted alkalis and even diluted mineral acids and aromatic hydrocarbons

\- not suitable for ketones, chlorinated hydrocarbons and phenols

H. Polyethylene (PE)

+ stands acids, alkalies and water solutions of salts and many organic solvents

\- not suitable for strong oxygen acids.

I. Polytetrafluoriethene (PTFE), Teflon

+ stands almost all chemicals

\- not suitable for liquid sodium and fluoride compounds

J. Fluoroelastomer, rubber, Viton

+ best chemical resistance of rubbers

K. Nitrile butadiene rubber (NBR)

+ stands well oil and gasoline

- not suitable for oxidative materials

L. Ethylene propylene diene monomer (EPDM)

+ stands well for reactive chemicals

- not suitable for oils and fats

M. Chlorosulfonated polyethylene synthetic rubber (CSM), Hypalon

+ stands many types of chemicals, even ozone and is weatherproof

- not suitable for solvents, oils and gasoline.

More information about chemical compatibility see Graco's and Ansell' databases:http://www.graco.com/content/dam/graco/ipd/literature/misc/chemical-compatibilityguide/Graco_ChemCompGuideENB.pdfhttp://www.ppe.ansell.com.au/chemical-glove-guide

5.2. Chemical accidents, consequences and lessons learnt

5.2.1. General

5.2.1.1. Course objectives/identification

The objectives of the course are as follows:

- to learn to know what kind of reasons typically cause great chemical disasters
- to learn to know what chemical typically are involved in chemical accidents
- to learn to know what kind of consequences can be as a result of chemical accidents
- to learn to know what we can learn from chemical accidents happened – lessons learnt

5.2.1.2. Course outcomes

As the outcomes of this course could be mentioned, among other things, the following:

- to know what chemicals typically cause chemical accidents

- to know typical reasons for chemical accidents on the base of lessons learnt
- to know how chemical accidents could be prevented in advance
- to get a good data base of typical chemical accident reports

5.2.1.3. Course terminology

- **BLEVE** Boiling Liquid Expanding Vapor Explosion
- **deflagration** explosion, no shock wave, low to fast burning
- **detonation** explosion with a shock wave, very high velocity of burning
- **dynamic accident** happens during longer time and consequences extent to larger area
- **ppm** concentration of part per million
- **LC50** lethal concentration, a measure of acute toxicity
- **LD50** lethal dose, a measure of acute toxicity
- **LPG** Liquefied Petroleum Gas, normally a mixture of propane and butane
- **MTBE** Methyl tert-butyl ether
- **PCB** Poly Chlorinated Biphenyl
- **static accident** happens fast and consequences form in few minutes
- **TNT** trinitrotoluene, explosive

5.2.1.4. Classification

Classification is a part of chemical accidents.

5.2.1.5. Operation (how it is used)

This training module includes theory and description of typical chemical accidents, their reasons and consequences both chemical accidents reports. After studying the text section there is a training section about questions to be answered (Appendix 1).

5.2.1.6. Pros. and Cons.

A. Pros.

Same kind of chemicals react more or less at the same way. That is why it is possible to prevent chemical accidents by taking suitable precautions in advance.

Accident reports from real chemical accidents provide important information how same kind of failures could be prevented.

B. Cons.

Each chemical accident is unique and depends of many different factors that cannot be always estimated. That is why it is dangerous to simplify too much even same kind of disasters.

5.2.2 Definition of chemical accidents

Chemical accidents could be determined as accidents where hazardous chemicals have been involved.

Chemical accidents can be grouped by different ways, like:

- Static or dynamic accidents
- Accidents of toxic or flammable gases or environmental accident
- Accidents on transportation, storage and processing of chemicals
- Fires, explosions or leaks

5.2.3. Types of chemical accidents

5.2.3.1. Static or dynamic accident [1]

A. Static accident

Typical for this kind of accident is that

- it happens fast and consequences and damages can be seen in few minutes after accident started
- it is restricted to a certain area
- typical accident type is explosion

B. Dynamic accident

Typical for static accident is that

- It happens during longer time and extend to larger area
- consequences and damages are born during a longer time (escalation)
- typical accident type is leaks of toxic gases or chemical leaks into watercourses

5.2.3.2. Accidents of toxic or flammable gases or environmental accident

A. Accidental leaks of toxic gases

- These accidents are most typical for pressure liquefied toxic gases like (ammonia, sulphur dioxide and chlorine)
- An example of toxicity of this kind of gases is given below [2]

Example 1: A tanker transporting sulphur dioxide (58 t) got a hole of 40 mm. SO2 flows away when a wind velocity is 2 m/s. In few minutes the lethal concentration can reach 300 m from the leaking point. It is not possible to be outdoors at the distance of 600 m. Later the lethal concentration can spread up to few kilometres.

- The world's worstindustrial disaster, Bhopal's gas leak incident in India is described in Case Nr 1.

B. Accidental leaks of flammable gases

- These accidents are most typical for pressure liquefied flammable gases like (propane, butane and natural gas methane)
- Examples of fire and explosion risk related to these chemicals are given below [2-3-4]

Example 2: LPG is leaking from a hole of 75 mm and a wind velocity is 2 m/s. It is estimated that a gas cloud can ignite even at the distance of 150 m from the leaking point. When the gas cloud explodes, a pressure wave caused by a deflagration will break windows at the distance of 400 m and damage buildings up to 200 meters.

Example 3: A great hole of a diameter of 1 m2 is borne on a LPG tank of a volume of 100 m3, f.ex. as a result of sabotage. Propane cloud is formed very fast and it is flammable to the extent of 250 m. In case the gas cloud ignites, burns of third grades can be obtained even at the distance of 400 m. As a result of pressure wave windows break up to 1000 meters' distance and buildings at the distance of 450 m.

Example 4: LPG tank is in fire and pressure increases inside. Heated metal softens and the tank ruptures, the content of the tank will expand, vaporize and explode. What happens is called BLEVE phenomenon (Boiling Liquid Expanding Vapor Explosion). BLEVE causes pressure damages, ignites fires and throw tank pieces up to many kilometres' distance.

Figure.5.8. BLEVE explosion of LPG Tank [5].

- It can be roughly said that hydrocarbons C3 –C4 cause about 40 % of accidents of flammable gases or liquids, and that propane is seems to be about 30 times more dangerous than gasoline [3]. It is worth mentioning that BLEVE explosion is possible in tanks of flammable liquids as well.
- Natural gas explosions are typical in underground tanks
- See Case Nr 2

C. Environmental accidents

- These accidents can be result of rather small leaks of hazardous chemicals in the environment
- Chemical leaks into the environment can very easily destroy nature, vegetation and animals
- As liquid or solid they normally pollute the soil, but liquids with small viscosity can very easily penetrate into groundwater and pollute it like water soluble additive of gasoline (MTBE); f. ex. 1 liter of MTBE in groundwater can make a half a million litres of water non-drinkable
- Spreading of chemicals in soil depends mainly on its viscosity, but also the soil type, f.ex. in sand chemical moves vertically 1-500 m/d, in silt 0.1-5 cm/d, but in clay 0.0001-0.5 cm/d [3]
- underground fuel tanks pose a special threat for groundwater, because their leak can be hard to observe
- liquids leaked into water courses can be divided into four group on the base of their behaviour in water [6]

I Liquids that are water soluble and heavier than water

II Liquids that are water soluble and lighter that water

III Liquids that are not water soluble and lighter that water

IV Liquids that are not water soluble and heavier than water

Group I: includes corrosives, like acids and bases (e.g. sulphuric acid, sodium hydroxide, nitric acid, hydrochloric acid); decrease pH of the water causing fish deaths, spoil drinking water etc.; become diluted with time; cannot be recovered; as a response could be liming

Group II: includes mainly alcohol or ketone based flammable liquids (e.g. ethanol, propanol, methanol, acetone); vaporize easily and can create flammable air mixture above water surface; not so toxic as chemicals in group I; become diluted with time; cannot be recovered; as response isolation of flammability area

Group III: includes oil based flammable liquids (e.g. heating oil, gasoline, xylene, benzene, hexane, acrylnitrile); floats on water; as response booming, adsorption, pumping, skimming, and other oil spill response methods; possible environmental damages are caused for plants and organisms of surface water

Group IV: includes manly toxic chemicals (e.g. phenol, chlorophenol, impregnating substances, carbon disulphide); sink to the bottom and dissolves very slowly into water; as response could be pumping or excavating from to bottom; to prevent long term environmental impacts, something has to be done (See Case Nr 3).

5.2.3.3. Accidents on transportation, storage and processing of chemicals

A. Transportation accidents

- Chemical accidents fire brigades typically response to are transportation accidents
- It is logical (statistically correct) that chemicals that are most commonly transported are also the most frequently involved into transportation accidents of chemicals
- According to inquiry made in Finland during preparation of Tokeva instructions very common materials cause most of the 440 chemical accidents studied from the time period of 1988 - 1992 [9]
  - ✓ 10 most common chemicals caused 60 % of chemical accidents
  - ✓ 24 most common chemicals caused 75 % of chemical accidents

✓ 62 most common chemicals caused 93 % of chemical accidents

Table.5.1. Chemical accidents during 1988 – 1992 [7] (24 chemicals which have caused accidents based on the TOKEVA inquiry).

diesel and fuel oil	76
liquefied petroleum gas	36
petrol	34
sulphuric acid	29
anhydrous ammonia	16
chlorine	16
nitric acid	14
hydrochloric acid	12
town gas	11
sodium hydroxide	9
oxygen	8
hexane	8
resin	7
ethyl alcohol	6
freon	6
sulphur	6
xylene	5
natural gas condensate	5
methanol	4

PCB	4
explosives	4
styrene	4
toluene	4
hydrogen	4

- Accidents on storage and processing of chemicals [8]
- During 1972-1987 there happened in Finnish industry accidents as follows (shares in parenthesis):
  - ✓ pulp and paper mills (31%), oil refineries and petrochemical industry (21%)
  - ✓ most common reasons were technical errors (39%), human errors (26%) and process failures (25%)

5.2.3.4. Fires, explosions or leaks

A. Fires

Fires can be classified by the following manner [9].

- Pool fires, 800 – 900 °C
- Jet fires, pressurized leak, 1200 °C
- Fire balls, e.g. in case of LPG tank rupture, > 1000 °C
- Gas fires, gas-air mixture is inside flammability range, burning velocity 0,5 – 2 m/s

B. Explosions

Explosions can be classified by the following manner [9].

- Mechanical explosion (e.g. rupture of pressure vessel, pressure 4-5 times filling pressure)
- Chemical explosion (e.g. dynamite)
- Nuclear explosion (e.g. fission, fusion)

Explosions can also be classified on the base of their nature [10].

- Detonation (detonation velocity 1500-8000 m/s, peak pressure 20 bar)
- Deflagration or swish (reaction velocity 0,1 – 1500 m/s)

When calculating consequences of explosions, the following classification can be done [9].

- Explosions in enclosed space (pressure 8-9 bar)
- Explosions in free space (gas amount 10-15 tons)

Other explosion types:

- BLEVE
- Powder explosions
- Chemical processes (exothermal reaction get out of control; e.g. cooling failure)

C. Leaks

- There are three different cases according to state:

✓ Gas leak

✓ Liquid leak

✓ Solid leak

- Danger area is generally largest for gas leaks (for toxic gases even many kilometres, for flammable gases few hundred meters)
- Precondition for gas leak is that tank pressure is higher than in its surroundings; sound of leak reminds that of a jet engine
- Gas flow reaches the speed of sound, 333 m/s, when pressure is about 2 bars
- The higher is gas flow, the more effective is dilution of gas into air because of mixing
- When flammable gas leaks, it can ignite at the distance of 250 x D, where D is a diameter of the discharge opening; a recommended safety distance is 500 x D
- When flammable gas leaks as liquid, it forms a spray, that can ignite at the distance of 1000 x D [13]
- It is possible to estimate spreading of gas cloud by computer programs (e.g. Escape in Finland) that consider weather conditions
- Danger area varies even 4-5 fold depending on stability class; the greatest danger area concerns calm air; sunshine and strong wind decrease danger area

✓ The most important gas leaks concern a) Leaks of compressed gases

✓ and Pressure liquefied gases

C.1. Leaks of compressed gases

- As a result of leak the tank pressure and mass flow decrease

C.2. Leaks of pressure liquefied gases

- There is both gas and liquid in the tank
- The tank pressure equals so called the vapour pressure
- When gas leaks, its temperature decreases slowly down to the boiling point of the gas, and then the vapour pressure is same as the atmospheric pressure (so called adiabatic vaporization)
- Gas plume is visible in the vicinity of liquid leak (the length of plume is about 10 m for a large leak, but about 1 meter for a small leak)
- The mass flow of liquid leak is about 15-20 times greater than in gas leak
- When liquid drops still vaporize a temperature can decrease even below the boiling point (f. ex. for ammonia even down to -70°C)

5.2. Consequences of chemical accidents

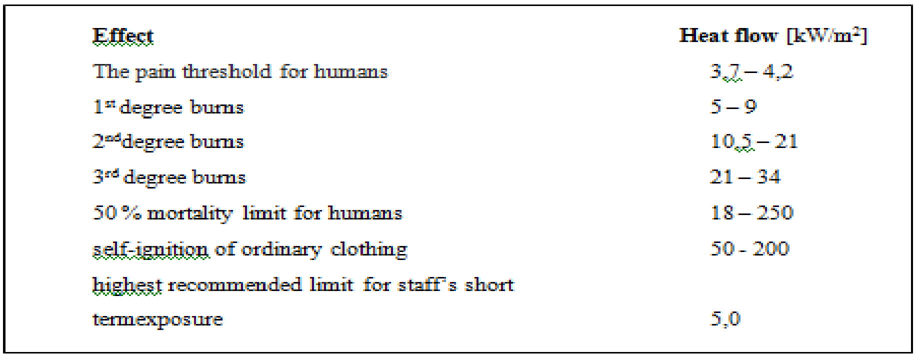
Chemical accident consequences can be divided into the following categories:

- burns
- explosion damages
- other health effects
- environmental impacts

5.2.1. Burns

Man does not withstand well heat radiation, as can be seen from Table 5.2.

Table.5.2. Effect of thermal heat radiation to humans [9].

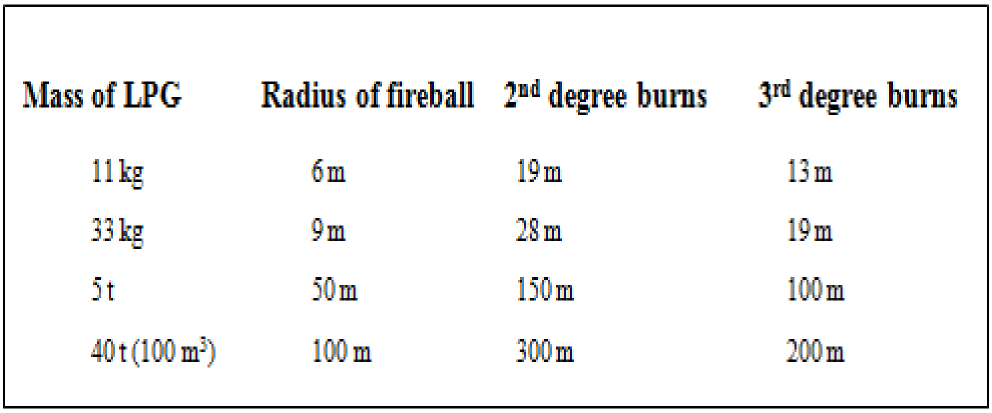


Effect	Heat flow [kW/m^2]
The pain threshold for humans	3,7 – 4,2
1st degree burns	5 – 9
2nd degree burns	10,5 – 21
3rd degree burns	21 – 34
50 % mortality limit for humans	18 – 250
self-ignition of ordinary clothing	50 - 200
highest recommended limit for staff's short termexposure	5,0

Values given in the Table.5.2 does not concern unprotected skin, because 1, degree burns can already be caused by heat radiation of 1 kW/m^2, corresponding to a warm summer day.

In case of rupture of LPG tank a surface temperature of formed fireball exceeds 1000 °C. So 3rd degree burns can be obtained at a distance of 2 x r and 2nd degree burns at a distance 3 x r (r = a radius of fireball). At the distance of 2 x r combustible surfaces also ignite.

Table.5.3. Burns caused by fireball as a function of LPG mass [6].



Mass of LPG	Radius of fireball	2nd degree burns	3rd degree burns
11 kg	6 m	19 m	13 m
33 kg	9 m	28 m	19 m
5 t	50 m	150 m	100 m
40 t (100 m^3)	100 m	300 m	200 m

.

The radius (r) of the Table 3 is calculated from the equation (1).

$$r = 2{,}9 \text{ x } (m)^{1/3}, \qquad (1)$$

where m = mass of LPG [kg]

r = radius of fireball [m]

The maximum size of a fireball formed in a Bleve explosion can be calculated from the equation (2). [12]

$$D_{max} = 5{,}25 \text{ m}^{\,0{,}314}, \qquad (2)$$

where

D_{max} = maximum size of a fireball [m]

m = mass of LPG [kg]

Example 6. Calculate a size of fireball formed when a half-full propane tank (1600 m^3) ruptures in Bleve explosion (f. ex. Mexico City, 1984).

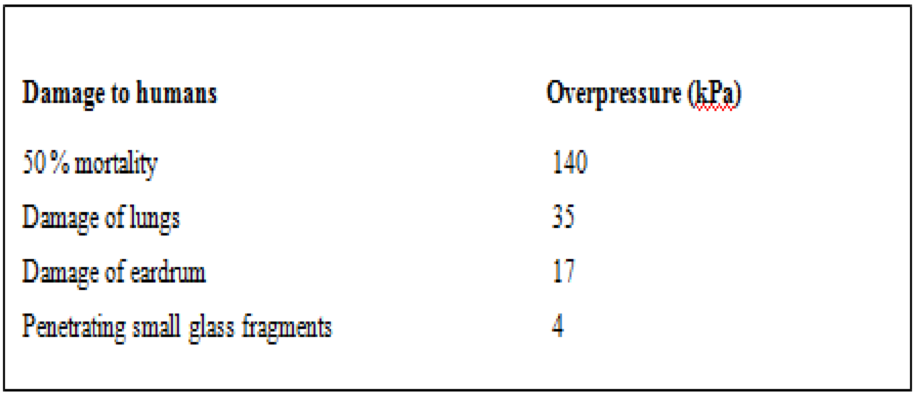
Mass of propane = 0,5 x 1600 m^3 x 510 kg / m^3 = 408000 kg

D_{max} = 5,25 x $(408000)^{0,314}$ = about **300 m**

5.2.2. Explosion damages

Explosion damages are formed both from a pressure wave and missiles. Man does not withstand well heat overpressure, as can be seen from Table.5.4.

Table.5.4. Effect of overpressure to humans [7-11].



Damage to humans	Overpressure (kPa)
50 % mortality	140
Damage of lungs	35
Damage of eardrum	17
Penetrating small glass fragments	4

Values are only indicatives.

Missiles from a tank explosion can flow very far. When gas cylinders and heated tanks explode, they normally flow in the direction of their longitudinal axis. So they should not be approached from end hand. Starting velocity for an explosive gas cylinder is 60 m/s. When a LPG tank (100 m3) explodes, normally 1 – 4 missiles are formed and they fly to less than 200 meters' distance. A half of tank can fly like a rocket much further [11].

5.2.3. Other health effects

Health hazardous substances can be classified as highly toxic (T+), toxic (T), harmful (Xn), irritating (Xi) or corrosive (C).

Humans can be exposed to hazardous substances via different routes:

- Eyes, nose, mouth, wounds, skin (f. ex. solvents)
- Poisonings can be classified into acute or chronic [11]
- Acute poisoning causes symptoms immediately (f. ex. chlorine) or during the next few hours, but chronic poisoning not before days (f. ex. nitric oxides), weeks or even years (f. ex. benzene) after exposure.

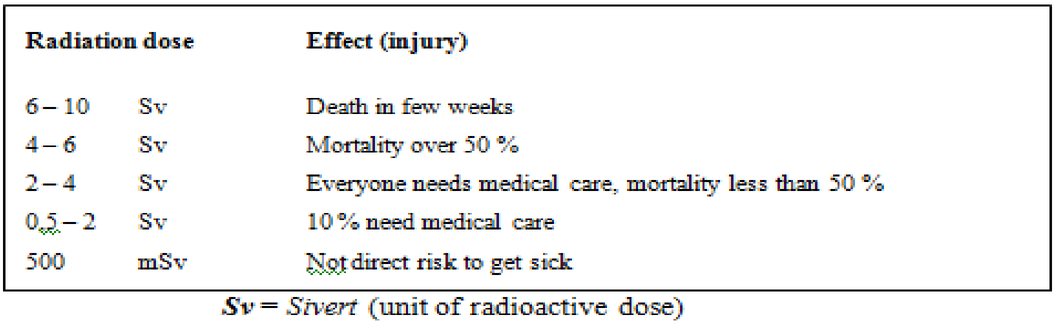
- Table 5.5 shows effects of common toxic gases (ammonia, sulphur dioxide, chlorine) in case of sudden rupture of tanks (f. ex. explosion of sabotage)

Table. 5.5. Injuries caused by sudden rupture of toxic gases to humans. Temperature 15°C, wind speed 3 m/s and weather type neutral [14].

Size of storage (t)	At what distances (km) distances different injuries are borne								
	Lethal injury			**Severe injury**			**Mild injury**		
	Cl_2	O_2	NH_3	Cl_2	O_2	NH_3	Cl_2	SO_2	NH_3
5	<0,5	<0,2	<0,2	0,5 – 1	<0,4	<0,2	3 – 4,5	0,4 - 0,7	<0,4
10	0,5	<0,2	<0,2	,5	<0,5	<0,3	4 – 5	1	<0,5
25	0,5 –1,5	0,4	0,2	2- 3	0,5 - 1	<0,5	6 – 7,5	1 - 2	0,7 – 1
50	1 – 3	0,5	0,3	3 - 6		0,4 - 1	8 – 12	1,2 – 2,6	– 1,5
100	1 – 5	0, 5 – 1	0,2 – 0,5	4 – 10	– 2	0,5 – 1,5	2 – 16	1,5 – 3	– 2
500	3 – 9	– 2	0,5 – 1,5	8 – 20	– 3,5	1 – 2,5	24 – 30	3 – 5,5	2 – 3,5
1000	6 – 13	– 3	0,7 – 2	2 – 27	2,5 – 5	1,5 – 3,5	34 – 44	4 – 7	2 – 5

- In connection of many chemical fires huge amounts of toxic gases are formed and they spread to long distances
- F. ex. fires of fertilizers, insecticides, plant pesticides, halogenated hydrocarbons, landfills
- Damages caused by radiation depend on dose according to the Table 5.6.

Table.5.6. Health Injuries to Humans as a Function of Radiation Dose [15].



Radiation dose		**Effect (injury)**
6 – 10	Sv	Death in few weeks
4 – 6	Sv	Mortality over 50 %
2 – 4	Sv	Everyone needs medical care, mortality less than 50 %
0,5 – 2	Sv	10 % need medical care
500	mSv	Not direct risk to get sick

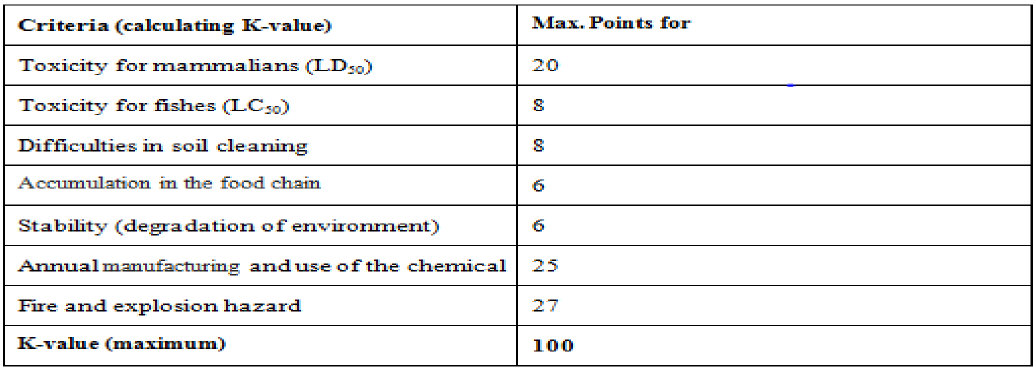
Sv = *Sivert* (unit of radioactive dose)

5.2.4. Environmental impacts

It is not easy to estimate environmental impacts, because at worst they concern almost permanent the destruction of our environment (f.ex. pollution of groundwater). On the other hand, effects and consequences can be seen only in the future concerning both the environment and potential illness of humans. There are many things and values associated with the environment that cannot be measured by human means (f.ex. in money).

Environmental hazard can be estimated by Gesamp's K–value, where the following factors are used as criteria [16] See Table.5.7.

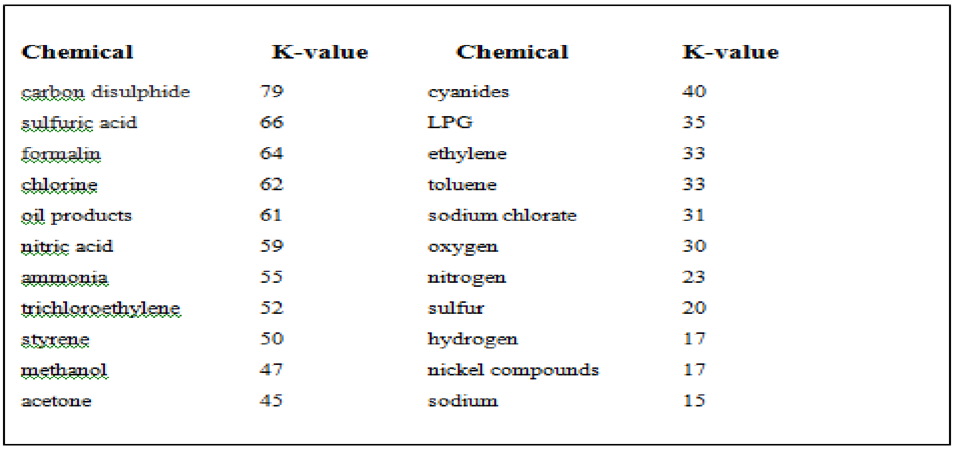
Table.5.7. Criteria for K-Value calculation.



Criteria (calculating K-value)	Max. Points for
Toxicity for mammalians (LD_{50})	20
Toxicity for fishes (LC_{50})	8
Difficulties in soil cleaning	8
Accumulation in the food chain	6
Stability (degradation of environment)	6
Annual manufacturing and use of the chemical	25
Fire and explosion hazard	27
K-value (maximum)	**100**

On the base of K-value a chemical is the more dangerous to the environment, the higher the K-value is. There have been listed K-values of some chemicals in the Table 8. It can be seen that very usual and commonly transported (f. ex. flammable liquids) cause a significant risk to the environment.

Table.5.8. Environmentally dangerous chemicals on the base of K-Value [16] (See case Nr 4).



Chemical	K-value	Chemical	K-value
carbon disulphide	79	cyanides	40
sulfuric acid	66	LPG	35
formalin	64	ethylene	33
chlorine	62	toluene	33
oil products	61	sodium chlorate	31
nitric acid	59	oxygen	30
ammonia	55	nitrogen	23
trichloroethylene	52	sulfur	20
styrene	50	hydrogen	17
methanol	47	nickel compounds	17
acetone	45	sodium	15

5.2.5. Chemical accident reports

5.2.5.1. Case Nr 1. Bhopal toxic gas leak in India

The Bhopal disaster, also referred to as the Bhopal gas tragedy, was a gas leak incident in India, considered the world's worstindustrial disaster [1].

It occurred on the night of 2–3 December 1984 at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, Madhya Pradesh. Over 500,000 people were exposed to methyl isocyanate (MIC) gas and other chemicals. The toxic substance made its way into and around the shanty towns located near the plant [2].

Estimates vary on the death toll. The official immediate death toll was 2,259. The government of Madhya Pradesh confirmed a total of 3,787 deaths related to the gas release [3]. A government affidavit in 2006 stated that the leak caused 558,125 injuries, including 38,478 temporary partial injuries and approximately 3,900 severely and permanently disabling injuries.[4] Others estimate that 8,000 died within two weeks, and another 8,000 or more have since died from gas-related diseases [5].

The cause of the disaster remains under debate. The Indian government and local activists argue that slack management and deferred maintenance created a situation where routine pipe maintenance caused a backflow of water into a MIC tank triggering the disaster. Union Carbide Corporation (UCC) contends water entered the tank through an act of sabotage [17].

Photograph.5.11. Bhopal gas disaster girl, the burial of one iconic victim of the gas leak.

5.2.5.2. Case Nr 2. San Juanico disaster (LPG) in Mexico

The San Juanico disaster was an industrialdisaster caused by a massive series of explosions at a liquid petroleum gas (LPG) tank farm in San Juanico, Mexico (outside of Mexico City, Mexico) on 19 November 1984 [1]. The explosions consumed 11,000 m3 of LPG, representing one third of Mexico City's entire liquid petroleum gas supply. The explosions destroyed the facility and devastated the local town of San Juan Ixhuatepec, with 500–600 people killed, and 5000–7000 others suffering severe burns [2]. The San Juanico disaster was one of the deadliest industrial disasters in world history [18].

Photograph.5.12. In the San Juanico disaster 54 of these spherical typeliquid petroleum gas (LPG) containers exploded.

5.2.5.3. Case Nr 3. Sandoz chemical spill in Switzerland

The Sandoz chemical spill was a major environmental disaster caused by a fire and its subsequent extinguishing at Sandoz agrochemical storehouse in Schweizerhalle, Basel-Landschaft, Switzerland, on 1 November 1986, which released toxic agrochemicals into the air and resulted in tons of pollutants entering the Rhine river, turning it red [1]. The chemicals caused a massive mortality of wildlife downstream, killing among other things a large proportion of the European eel population in the Rhine [2], although the situation subsequently recovered within a couple of years [3]. The stored chemicals included, urea, fluorescent dye, organophosphate insecticides, mercury compounds and organochlorines [4]. Among the major resulting water pollutants were dinitro-ortho-cresol, the organophosphate chemicals propetamphos, parathion, disulfoton, thiometon, etrimphos and fenitrothion, as well as the organochlorine metoxuron [19].

Photograph.5.13. Dead eel had to be collected from the rhine after the disaster [20].

5.2.5.4. Case Nr 4. Seveso disaster in Italy

The Seveso disaster was an industrial accident that occurred around 12:37 pm on July 10, 1976, in a small chemical manufacturing plant approximately 20 kilometres (12 mi) north of Milan in the Lombardy region of Italy. It resulted in the highest known exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in residential populations which gave rise to numerous scientific studies and standardized industrial safety regulations. The EU industrial safety regulations are known as the Seveso II Directive [21].

Photograph.5.14. A child Afflicted with Chloracne, one of the Results of the TCDD Gas Released during the Seveso Disaster [22].

5.3. Chemical accidents, accident analysis

5.3.1. Objective of the course

It is important to identify and describe anatomy of chemical accidents for improvement of preparedness for similar occasions. This course contains several tools for analysing accident processes.

A chemical accident is the unintentional release of one or more hazardous substances which could harm human health or the environment. Chemical hazards are systems where chemical accidents could occur under certain circumstances. Such events include fires, explosions, leakages or releases of toxic or hazardous materials that can cause people illness, injury, disability or death.

While chemical accidents may occur whenever toxic materials are stored, transported or used, the most severe accidents are industrial accidents, involving major chemical manufacturing and storage facilities. The most significant chemical accident in recorded history was the 1984 Bhopal disaster in India, in which more than 3,000 people were killed after a highly toxic vapour, (methyl isocyanate), was released at a Union Carbide Pesticides factory.

Efforts to prevent accidents range from improved safety systems to fundamental changes in chemical use and manufacture, referred to as primary prevention or inherent safety [1].

5.3.2. Identification of the course

In the United States, concern about chemical accidents after the Bhopal disaster led to the passage of the 1986 Emergency Planning and Community Right-to-Know Act. The EPCRA requires local emergency planning efforts throughout the country, including emergency notifications. The law also requires companies to make publicly available information about their storage of toxic chemicals. Based on such information, citizens can identify the vulnerable zones in which severe toxic releases could cause harm or death.

In 1990, the Chemical Safety and Hazard Investigation Board was established by Congress, though the CSB did not become operational until 1998. The Board's mission is to determine the root causes of chemical accidents and issue safety recommendations to prevent future Safety Performance Indicators. It also organizes workshops on a number of issues related to preparing for, preventing, and responding to chemical accidents [1].

In the European Union, incidents such as the Flixborough disaster and the Seveso disaster led to legislation such as the Seveso Directive and Seveso planning and provide for safety reports to local authorities. Many countries have organisations that can assist with substance risk assessment and emergency planning that is required by a wide variety of legislation, such as the National Chemical Emergency Centre in the UK, Brandweerinformatiecentrum voor gevaarlijke stoffen/Fire service information centre for dangerous goods in Belgium.

In the UK, the UK Chemical Reaction Hazards Forum publishes reports of accidents on its web site. These accidents were, at the time, minor in nature, but they could have escalated into major accidents. It is hoped that publishing these incidents will prevent "Re-inventing the Wheel" [1].

5.3.3. Outcomes of the course

Accident analysis is carried out in order to determine the cause or causes of an accident or series of accidents so as to prevent further incidents of a similar kind. It is also known as accident investigation. It may be performed by a range of experts, including forensic scientists, forensic engineers or health and safety advisers. Accident investigators, particularly those in the aircraft industry, are colloquially known as "tin-kickers".

5.3.4. Accident analysis is performed in four steps

1. Fact gathering: After an accident happened a forensic process starts to gather all possibly relevant facts that may contribute to understanding the accident.

2. Fact Analysis: After the forensic process has been completed or at least delivered some results, the facts are put together to give a "big picture." The history of the accident is reconstructed and checked for consistency and plausibility.

3. Conclusion Drawing: If the accident history is sufficiently informative, conclusions can be drawn about causation and contributing factors.

4. Counter-measures: In some cases, the development of counter-measures is desired or recommendations have to be issued to prevent further accidents of the same kind.

There exist numerous forms of Accident Analysis methods. These can be divided into three categories:

1. Causal Analysis uses the principle of causality to determine the course of events: Though people casually speak of a "chain of events", results from Causal Analysis usually have the form of directed a-cyclic graphs – the nodes being events and the edges the cause-effect relations. Methods of Causal Analysis differ in their respective notion of causation.

2. Expert Analysis relies on the knowledge and experience of field experts: This form of analysis usually lacks a rigorous (formal/semiformal) methodological approach. This usually affects falsify-ability and objectivity of analyses. This is of importance when conclusions are heavily disputed among experts.

3. Organizational Analysis relies on systemic theories of organization: Most theories imply that if a system's behaviour stayed within the bounds of the ideal organization then no accidents can occur. Organizational Analysis can be falsified and results from analyses can be checked for objectivity. Choosing an organizational theory for accident analysis comes from the assumption that the system to be analysed conforms to that theory [2].

For getting practical view of chemical accident, look some example accident descriptions from Finland: http://tukes.fi/Tiedostot/vaaralliset_aineet/ohjeet/mahb-bulletin-no1-final.pdf

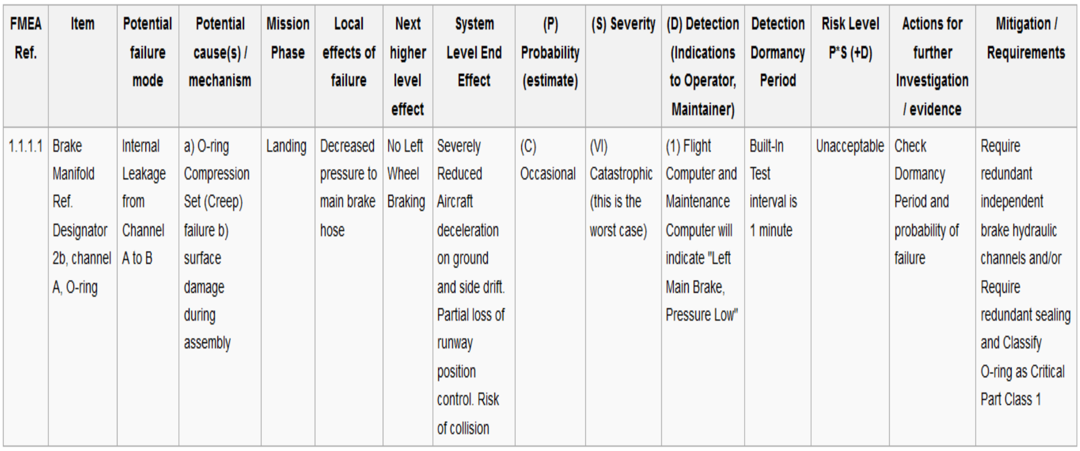
5.3.5. Classification and operation

5.3.5.1. FMEA failure mode and effect analysis

The FME(C)A is a design tool used to systematically analyse postulated component failures and identify the resultant effects on system operations. The analysis is sometimes characterized as consisting of two sub-analyses, the first being the failure modes and effects analysis (FMEA), and the second, the criticality analysis (CA). Successful development of an FMEA requires that the analyst include all significant failure modes for each contributing element or part in the system. FMEAs can be performed at the system, subsystem, assembly, subassembly or part level. The FMECA should be a living document during development of a hardware design. It should be scheduled and completed concurrently with the design. If completed in a timely manner, the FMECA can help guide design decisions. The usefulness of the FMECA as a design tool and in the decision-making process is dependent on the effectiveness and timeliness with which design problems are identified. Timeliness is probably the most important consideration. In the extreme case, the FMECA would be of little value to the design decision process if the analysis is performed after the hardware is built. While the FMECA identifies all part failure modes, its primary benefit is the early identification of all critical and catastrophic subsystem or system failure modes so they can be eliminated or minimized through design modification at the earliest point in the development effort; therefore, the FMECA should be performed at the system level as soon as preliminary design information is available and extended to the lower levels as the detail design progresses [2].

Remark: For more complete scenario modelling another type of Reliability analysis may be considered, for example fault tree analysis (FTA); a deductive (backward logic) failure analysis that may handle multiple failures within the item and/or external to the item including maintenance and logistics. It starts at higher functional / system level. An FTA may use the basic failure mode FMEA records or an effect summary as one of its inputs (the basic events). Interface hazard analysis, Human error analysis and others may be added for completion in scenario modelling.

Table.5.9. Example worksheet FMEA.

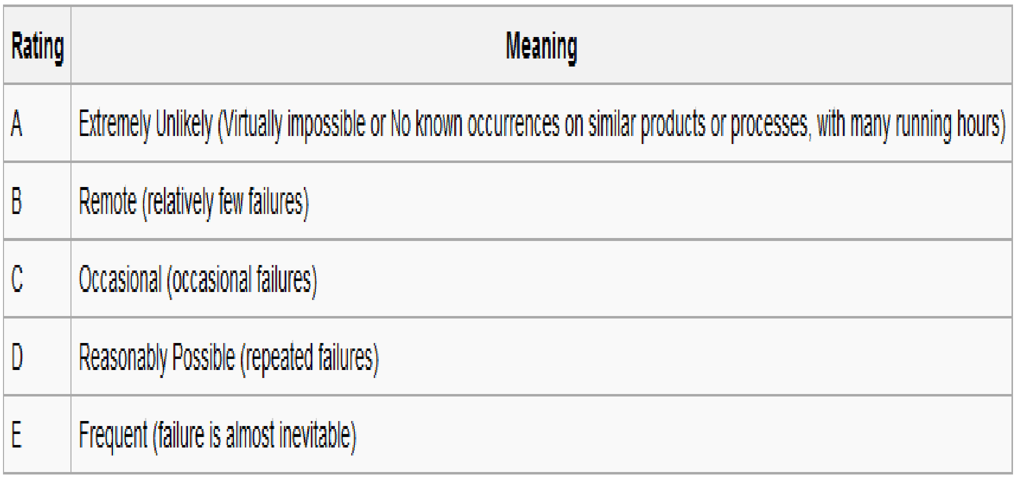


FMEA Ref.	Item	Potential failure mode	Potential cause(s) / mechanism	Mission Phase	Local effects of failure	Next higher level effect	System Level End Effect	(P) Probability (estimate)	(S) Severity	(D) Detection (Indications to Operator, Maintainer)	Detection Dormancy Period	Risk Level P*S (+D)	Actions for further Investigation / evidence	Mitigation / Requirements
1.1.1.1	Brake Manifold Ref. Designator 2b, channel A, O-ring	Internal Leakage from Channel A to B	a) O-ring Compression Set (Creep) failure b) surface damage during assembly	Landing	Decreased pressure to main brake hose	No Left Wheel Braking	Severely Reduced Aircraft deceleration on ground and side drift. Partial loss of runway position control. Risk of collision	(C) Occasional	(VI) Catastrophic (this is the worst case)	(1) Flight Computer and Maintenance Computer will indicate "Left Main Brake, Pressure Low"	Built-In Test interval is 1 minute	Unacceptable	Check Dormancy Period and probability of failure	Require redundant independent brake hydraulic channels and/or Require redundant sealing and Classify O-ring as Critical Part Class 1

A. Probability (P)

It is necessary to look at the cause of a failure mode and the likelihood of occurrence. This can be done by analysis, calculations / FEM, looking at similar items or processes and the failure modes that have been documented for them in the past. A failure cause is looked upon as a design weakness. All the potential causes for a failure mode should be identified and documented. This should be in technical terms. Examples of causes are: Human errors in handling, Manufacturing induced faults, Fatigue, Creep, Abrasive wear, erroneous algorithms, excessive voltage or improper operating conditions or use (depending on the used ground rules). A failure mode is given a Probability Ranking.

Table.5.10. Probability rating.

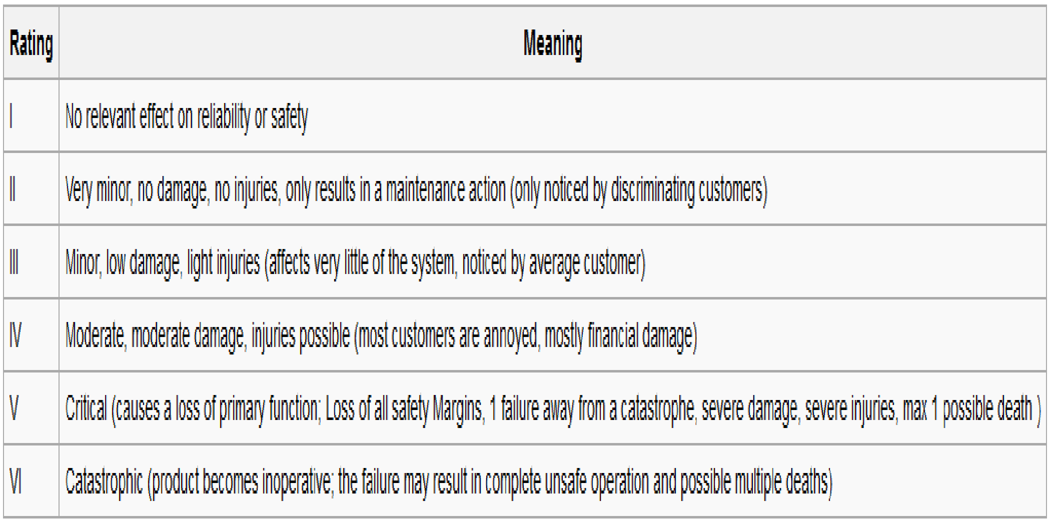


Rating	Meaning
A	Extremely Unlikely (Virtually impossible or No known occurrences on similar products or processes, with many running hours)
B	Remote (relatively few failures)
C	Occasional (occasional failures)
D	Reasonably Possible (repeated failures)
E	Frequent (failure is almost inevitable)

B. Severity (S)

Determine the Severity for the worst-case scenario adverse end effect (state). It is convenient to write these effects down in terms of what the user might see or experience in terms of functional failures. Examples of these end effects are: full loss of function x, degraded performance, functions in reversed mode, too late functioning, erratic functioning, etc. Each end effect is given a Severity number (S) from, say, I (no effect) to VI (catastrophic), based on cost and/or loss of life or quality of life. These numbers prioritize the failure modes (together with probability and delectability). Below a typical classification is given. Other classifications are possible.

Table.5.11. Severity rating.

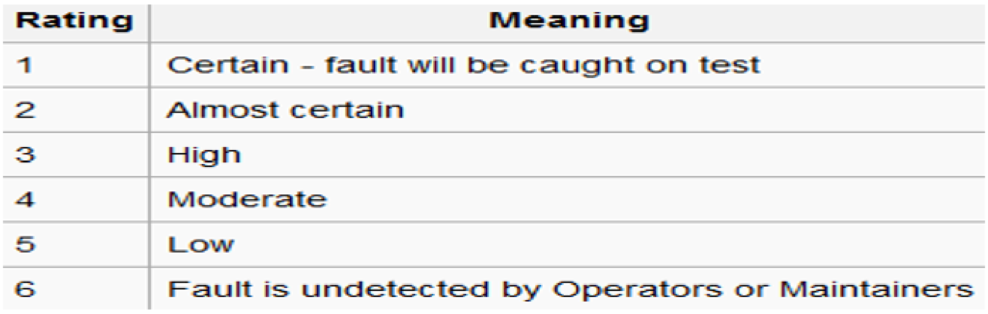


Rating	Meaning
I	No relevant effect on reliability or safety
II	Very minor, no damage, no injuries, only results in a maintenance action (only noticed by discriminating customers)
III	Minor, low damage, light injuries (affects very little of the system, noticed by average customer)
IV	Moderate, moderate damage, injuries possible (most customers are annoyed, mostly financial damage)
V	Critical (causes a loss of primary function; Loss of all safety Margins, 1 failure away from a catastrophe, severe damage, severe injuries, max 1 possible death)
VI	Catastrophic (product becomes inoperative; the failure may result in complete unsafe operation and possible multiple deaths)

C. Detection (D)

The means or method by which a failure is detected, isolated by operator and/or maintainer and the time it may take. This is important for maintainability control (Availability of the system) and it is especially important for multiple failure scenarios. This may involve dormant failure modes (e.g. No direct system effect, while a redundant system / item automatic takes over or when the failure only is problematic during specific mission or system states) or latent failures (e.g. deterioration failure mechanisms, like a metal growing crack, but not a critical length). It should be made clear how the failure mode or cause can be discovered by an operator under normal system operation or if it can be discovered by the maintenance crew by some diagnostic action or automatic built in system test. A dormancy and/or latency period may be entered.

Table.5.12. Detection rating.



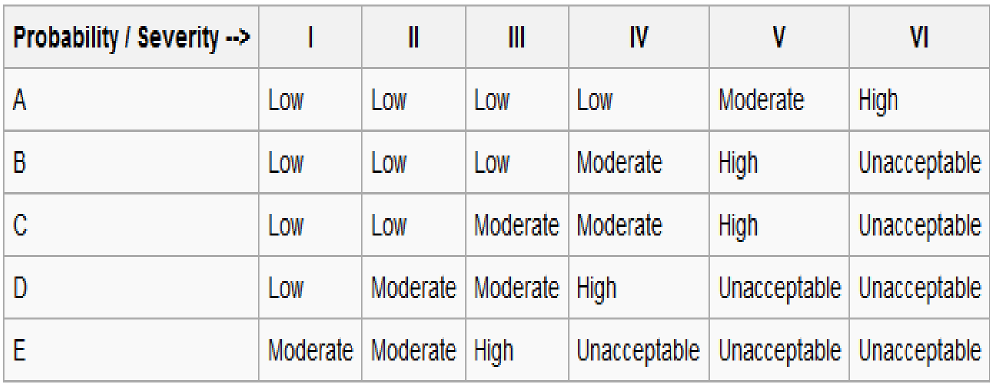
Rating	Meaning
1	Certain - fault will be caught on test
2	Almost certain
3	High
4	Moderate
5	Low
6	Fault is undetected by Operators or Maintainers

D. Risk level (P*S) and (D)

Risk is the combination of End Effect Probability and Severity where probability and severity includes the effect on non-delectability (dormancy time). This may influence the end effect probability of failure or the worst case effect Severity. The exact calculation may not be easy in all cases, such as those where multiple scenarios (with multiple events) are possible and delectability / dormancy plays a crucial role (as for redundant systems). In that case Fault Tree Analysis and/or Event Trees may be needed to determine exact probability and risk levels.

Preliminary Risk levels can be selected based on a Risk Matrix like shown below, based on Mil. Std. 882. The higher the Risk level, the more justification and mitigation is needed to provide evidence and lower the risk to an acceptable level. High risk should be indicated to higher level management, who are responsible for final decision-making.

Table.5.13. FMEA risk rating.



Probability / Severity -->	I	II	III	IV	V	VI
A	Low	Low	Low	Low	Moderate	High
B	Low	Low	Low	Moderate	High	Unacceptable
C	Low	Low	Moderate	Moderate	High	Unacceptable
D	Low	Moderate	Moderate	High	Unacceptable	Unacceptable
E	Moderate	Moderate	High	Unacceptable	Unacceptable	Unacceptable

5.3.5.2. Accimap analysis

The AcciMap Approach is a systems-based technique for accident analysis, specifically for analysing the causes of accidents and incidents that occur in complex socio technical systems [3].

The approach was originally developed by Jens Rasmussen as part of a proactive risk management strategy, but its primary application has been as an accident analysis tool.

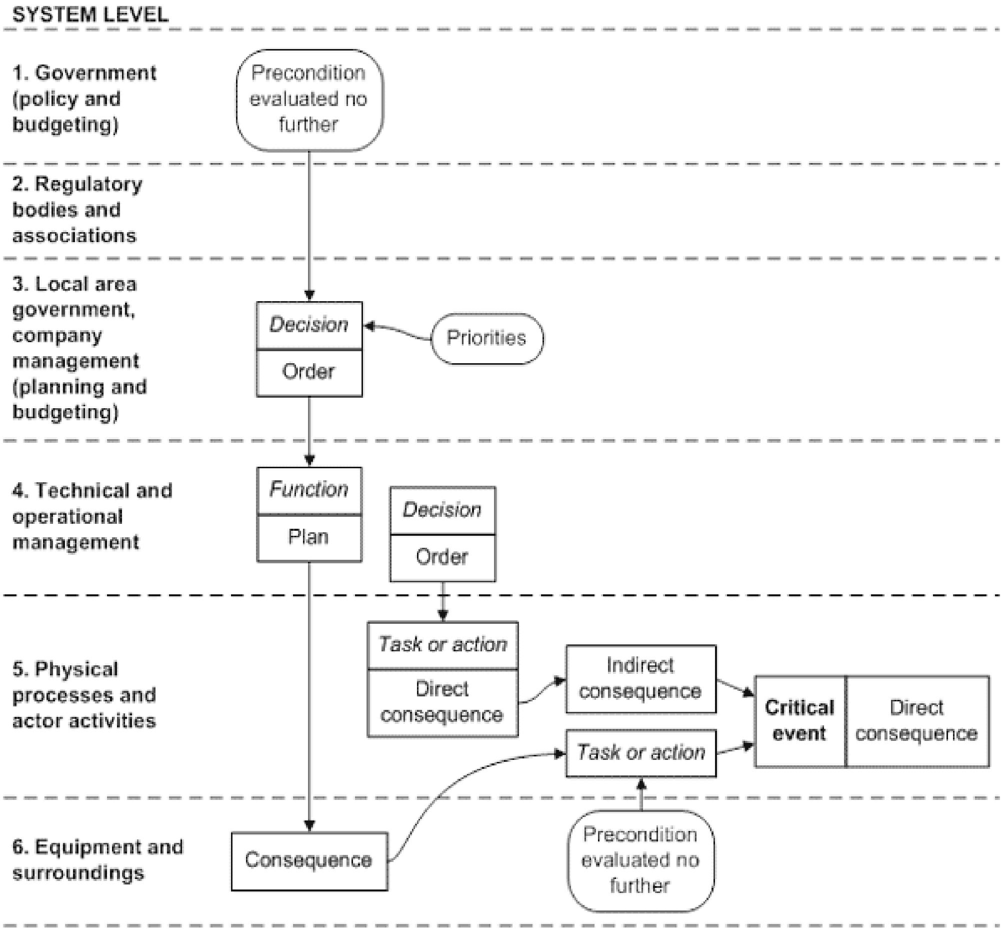
The approach is not domain-specific and has been used to analyse accidents in a range of industries including aviation, defence, oil and gas, public health, risk management, policing, and public health and rail transport. The method is used to analyse the contributing factors of accidents at all levels of the system, and can also be utilised to formulate safety recommendations [4].

The AcciMap approach is useful for uncovering how factors in the various parts of the system contributed to an accident, and for arranging those factors into a logical causal diagram that illustrates how they combined to result in that event. The method also promotes a systemic view of accident causation as the AcciMap diagram extends well beyond the most immediate causes of the event to reveal the full range of higher-level factors that contributed to the outcome (or failed to prevent it from occurring). It therefore assists analysts in understanding how and why an accident took place, and prevents attention from focusing disproportionately on the immediate causes (such as errors made by front-line workers), because the factors that provoked or permitted those factors are also revealed. The approach therefore helps to avoid blaming frontline individuals for accidents and leaving the factors that contributed to their behaviour unaddressed. In extending to consider contributing factors at governmental, regulatory and societal levels, the approach also has the capacity to capture and address high-level contributing factors that are typically excluded from accident analyses developed using other methods [5].

The AcciMap approach involves the construction of a multi-layered causal diagram in which the various causes of an accident are arranged according to their causal remoteness from the outcome (depicted at the bottom of the diagram). The most immediate causes are shown in the lower sections of the diagram, with more remote causes shown at progressively higher levels, so that the full range of factors that contributed to the event are modelled.

The precise format of the diagram varies depending on the purpose of analysis, but the lower levels typically represent the immediate precursors to the event, relating to the activities of workers and to physical events, processes and conditions that contributed to the outcome. The next highest levels typically represent company and organisational-level factors. The highest levels generally incorporate governmental or societal-level causal factors, which are external to the organisation(s) involved in the event. Compiling the multiple contributing factors and their interrelationships into a single logical diagram in this way helps analysts understand how and why the event took place and pinpoints problem areas that can be addressed to improve system safety [9].

Figure.5.9. Example accimap (http://www.ergonomicsblog.uk/accimap/).



5.3.5.3. Fault tree analysis

Fault tree analysis (FTA) is a top down, deductivefailure analysis in which an undesired state of a system is analysed using Boolean logic to combine a series of lower-level events. This analysis method is mainly used in the fields of safety engineering and reliability engineering to understand how systems can fail, to identify the best ways to reduce risk or to determine (or get a feeling for) event rates of a safety accident or a particular system level (functional) failure. FTA is used in the aerospace, nuclear power, chemical and process, pharmaceutical, petrochemical and other high-hazard industries; but is also used in fields as diverse as risk factor identification relating to social service system failure. FTA is also used in software engineering for debugging purposes and is closely related to cause-elimination technique used to detect bugs [6].

In aerospace, the more general term "system Failure Condition" is used for the "undesired state" / Top event of the fault tree. These conditions are classified by the severity of their effects. The most severe conditions require the most extensive fault tree analysis. These "system Failure Conditions" and their classification are often previously determined in the functional Hazard analysis [7].

A. Fault tree analysis can be used to

- understand the logic leading to the top event / undesired state.
- show compliance with the (input) system safety / reliability requirements.
- prioritize the contributors leading to the top event - Creating the Critical Equipment/Parts/Events lists for different importance measures.
- monitor and control the safety performance of the complex system (e.g., is a particular aircraft safe to fly when fuel valve x malfunctions? For how long is it allowed to fly with the valve malfunction?).
- minimize and optimize resources.
- assist in designing a system. The FTA can be used as a design tool that helps to create (output / lower level) requirements.
- function as a diagnostic tool to identify and correct causes of the top event. It can help with the creation of diagnostic manuals / processes.

FTA methodology is described in several industry and government standards, including NRC NUREG–0492 for the nuclear power industry, an aerospace-oriented revision to NUREG–0492 for use by NASA, SAEARP4761 for civil aerospace, MIL–HDBK–338 for military systems, IEC standard IEC 61025 is intended for cross-industry use and has been adopted as European Norm EN 61025.

Any sufficiently complex system is subject to failure as a result of one or more subsystems failing. The likelihood of failure, however, can often be reduced through improved system design. Fault tree analysis maps the relationship between faults, subsystems, and redundant safety design elements by creating a logic diagram of the overall system.

The undesired outcome is taken as the root ('top event') of a tree of logic. For instance, the undesired outcome of a metal stamping press operation is a human appendage being stamped. Working backward from this top event we might determine there are two ways this could happen: during normal operation or during maintenance operation. This condition is a logical OR. Considering the branch of occurring during normal operation perhaps we determine there are two ways this could happen: the press cycles and harms the operator or the press cycles and harms another person. This is another logical OR. We can make a design improvement by requiring the operator to press two buttons to cycle the machine—this is a safety feature in the form of a logical AND. The button may have an intrinsic failure rate—this becomes a fault stimulus we can analyse. When fault trees are labelled with actual numbers for failure probabilities, computer programs can calculate failure probabilities from fault trees. When a specific event is found to have more than one effect event, i.e. it has impact on several subsystems, it is called a common cause or common mode. Graphically speaking, it means this event will appear at several locations in the tree. Common causes introduce dependency relations between events. The probability computations of a tree which contains some common causes are much more complicated than regular trees where all events are considered as independent. Not all software tools available on the market provide such capability.

The Tree is usually written out using conventional logic gate symbols. The route through a tree between an event and an initiator in the tree is called a Cut Set. The shortest credible way through the tree from fault to initiating event is called a Minimal Cut Set.

Some industries use both fault trees and event trees. An Event Tree starts from an undesired initiator (loss of critical supply, component failure etc.) and follows possible further system events through to a series of final consequences. As each new event is considered, a new node on the tree is added with a split of probabilities of taking either branch. The probabilities of a range of 'top events' arising from the initial event can then be seen.

Classic programs include the Electric Power Research Institute's (EPRI) CAFTA software, which is used by many of the US nuclear power plants and by a majority of US and international aerospace manufacturers, and the Idaho National Laboratory's SAPHIRE, which is used by the U.S. Government to evaluate the safety and reliability of nuclear reactors, the Space Shuttle, and the International Space Station. Outside the US, the software Risk Spectrum is a popular tool for Fault Tree and Event Tree analysis and is licensed for use at almost half of the world's nuclear power plants for Probabilistic Safety Assessment [9].

B. Basic gates of a fault tree are the follows

OR gate the above output event occurs if either of the input lower level events occur

AND gate the above output event occurs if all of the input lower level events occur

TRANSFER gate transfer to/from another part of the fault tree

Events in a fault tree are associated with statisticalprobabilities. For example, component failures may typically occur at some constant failure rate λ (a constant hazard function). In this simplest case, failure probability depends on the rate λ and the exposure time t:

$P = 1 - \exp(-\lambda t)$

$P \approx \lambda t, \lambda t < 0.1$

A fault tree is often normalized to a given time interval, such as a flight hour or an average mission time. Event probabilities depend on the relationship of the event hazard function to this interval.

Unlike conventional logic gate diagrams in which inputs and outputs hold the binary values of TRUE (1) or FALSE (0), the gates in a fault tree output probabilities related to the set operations of Boolean logic. The probability of a gate's output event depends on the input event probabilities.

An AND gate represents a combination of independent events. That is, the probability of any input event to an AND gate is unaffected by any other input event to the same gate. In set theoretic terms, this is equivalent to the intersection of the input event sets, and the probability of the AND gate output is given by:

$P\ (A \text{ and } B) = P\ (A \cap B) = P(A)\ P(B)$

An OR gate, on the other hand, corresponds to set union:

$P\ (A \text{ or } B) = P\ (A \cup B) = P(A) + P(B) - P\ (A \cap B)$

Since failure probabilities on fault trees tend to be small (less than .01), $P\ (A \cap B)$ usually becomes a very small error term, and the output of an OR gate may be conservatively approximated by using an assumption that the inputs are mutually exclusive events:

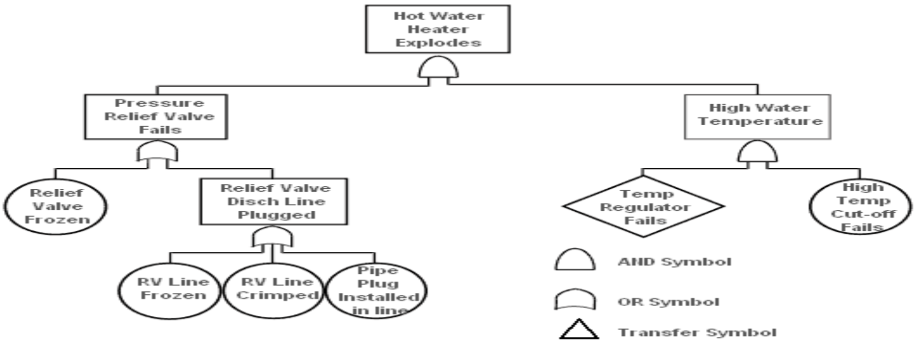
$P\ (A \text{ or } B) \approx P(A) + P(B),\ P\ (A \cap B) \approx 0$

An exclusive OR gate with two inputs represents the probability that one or the other input, but not both, occurs:

$P\ (A \text{ xor } B) = P(A) + P(B) - 2P\ (A \cap B)$

Again, since $P\ (A \cap B)$ usually becomes a very small error term, the exclusive OR gate has limited value in a fault tree [7].

Figure.5.10. Example fault tree (http://www.qualitytrainingportal.com/resources/problem-solving-tools/data-display-analysis/problem-solving_tools-fault_tree.htm).



5.3.5.4. Event tree

Event tree analysis (ETA) is a forward, bottom up, logical modelling technique for both success and failure that explores responses through a single initiating event and lays a path for assessing probabilities of the outcomes and overall system analysis. This analysis technique is used to analysed the effects of functioning or failed systems given that an event has occurred. ETA is a powerful tool that will identify all consequences of a system that have a probability of occurring after an initiating event that can be applied to a wide range of systems including: nuclear power plants, spacecraft, and chemical plants. This Technique may be applied to a system early in the design process to identify potential issues that may arise rather than correcting the issues after they occur. With this forward logic process use of ETA as a tool in risk assessment can help to prevent negative outcomes from occurring by providing a risk assessor with the probability of occurrence. ETA uses a type of modeling technique called event tree, which branches events from one single event using Boolean logic [8].

Performing a probabilistic risk assessment starts with a set of initiating events that change the state or configuration of the system. An initiating event is an event that starts a reaction, such as the way a spark (initiating event) can start a fire that could lead to other events (intermediate events) such as a tree burning down, and then finally an outcome, for example, the burnt tree no longer provides apples for food. Each initiating event leads to another event and continuing through this path, where each intermediate events probability of occurrence may be calculated by using fault tree analysis, until an end state is reached (the outcome of a tree no longer providing apples for food). Intermediate events are commonly split into a binary (success/failure or yes/no) but may be split into more than two as long as the events are mutually exclusive, meaning that they cannot occur at the same time. If a spark is the initiating event, there is a probability that the spark will start a fire or will not start a fire (binary yes or no) as well as the probability that the fire spreads to a tree or does not spread to a tree. End states are classified into groups that can be successes or severity of consequences. An example of a success would be that no fire started and the tree still provided apples for food while the severity of consequence would be that a fire did start and we lose apples as a source of food. Loss end states can be any state at the end of the pathway that is a negative outcome of the initiating event. The loss end state is highly dependent upon the system, for example if you were measuring a quality process in a factory a loss or end state would be that the product has to be reworked or thrown in the trash. Some common loss end states [7].

- Loss of Life or Injury/ Illness to personnel
- Damage to or loss of equipment or property (including software)

- Unexpected or collateral damage as a result of tests
- Failure of mission
- Loss of system availability
- Damage to the environment

The overall goal of event tree analysis is to determine the probability of possible negative outcomes that can cause harm and result from the chosen initiating event. It is necessary to use detailed information about a system to understand intermediate events, accident scenarios, and initiating events to construct the event tree diagram. The event tree begins with the initiating event where consequences of this event follow in a binary (success/failure) manner. Each event creates a path in which a series of successes or failures will occur where the overall probability of occurrence for that path can be calculated. The probabilities of failures for intermediate events can be calculated using fault tree analysis and the probability of success can be calculated from 1 = probability of success(ps) + probability of failure (pf). For example, in the equation 1 = (ps) + (pf) if we know that pf=.1 from fault tree analysis then through simple algebra we can solve for ps where ps = (1) - (pf) then we would have ps = (1) - (.1) and ps=.9.

The event tree diagram models all possible pathways from the initiating event. The initiating event starts at the left side as a horizontal line that branches vertically. the vertical branch is representative of the success/failure of the initiating event. At the end of the vertical branch a horizontal line is drawn on each the top and the bottom representing the success or failure of the first event where a description (usually success or failure) is written with a tag that represents the path such as 1s where s is a success and 1 is the event number similarly with 1f where 1 is the event number and f denotes a failure. This process continues until the end state is reached. When the event tree diagram has reached the end state for all pathways the outcome probability equation is written [9].

A. Steps to perform an event tree analysis

1. Define the system: Define what needs to be involved or where to draw the boundaries.

2. Identify the accident scenarios: Perform a system assessment to find hazards or accident scenarios within the system design.

3. Identify the initiating events: Use a hazard analysis to define initiating events.

4. Identify intermediate events: Identify countermeasures associated with the specific scenario.

5. Build the event tree diagram.

6. Obtain event failure probabilities: If the failure probability cannot be obtained use fault tree analysis to calculate it.

7. Identify the outcome risk: Calculate the overall probability of the event paths and determine the risk.

8. Evaluate the outcome risk: Evaluate the risk of each path and determine its acceptability.

9. Recommend corrective action: If the outcome risk of a path is not acceptable develop design changes that change the risk.

10. Document the ETA: Document the entire process on the event tree diagrams and update for new information as needed.

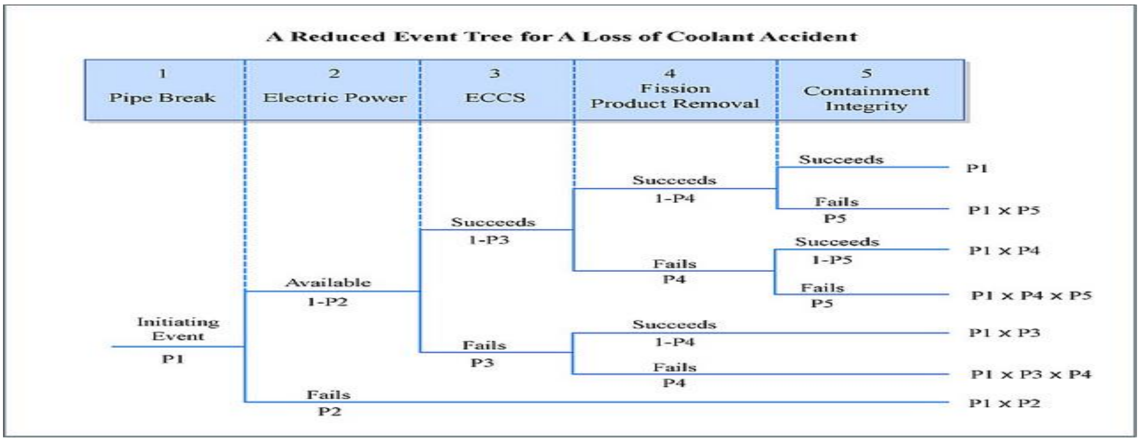
5.3.5.5. Mathematical concepts

1 = (probability of success) + (probability of failure)

The probability of success can be derived from the probability of failure.

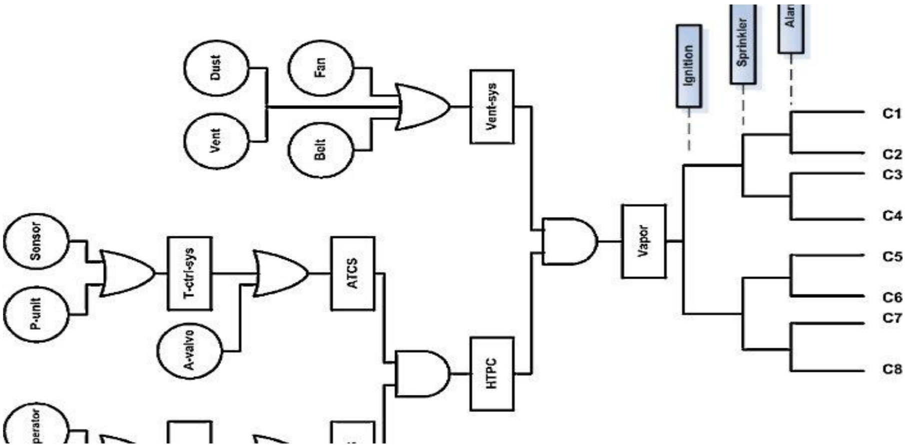
Overall path probability = (probability of event 1) X (probability of event 2) X (probability of event n....) [8].

Figure. 11. Event tree consists of questions about protection or security mechanisms and estimated probabilities for answers YES/NO. The sum of probabilities of each pair of answers is always 1: P(NO)+P(YES)=1 (https://www.flickr.com/photos/mitopencourseware/4749476344).



Link between fault tree and event tree can be seen in picture 5. Top accident (vapour) of fault tree is the beginning occasion of event tree.

Figure.5.12. Link from fault tree to event tree (https://www.linkedin.com/pulse/event-tree-analysis-eta-fault-fta-renyou-zhang).

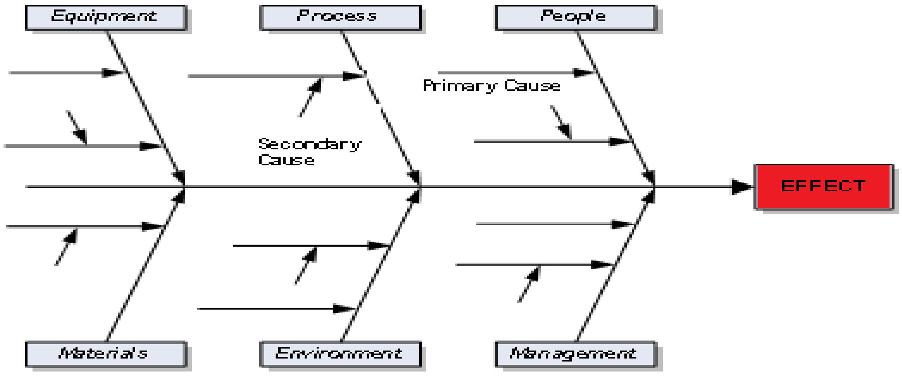


A. 5M, 7M (Management, Milieu, Man, Money, Method, Material, Machine, Measurement)- Fishbone, Ishikawa Diagram)

Ishikawa diagrams (also called fishbone diagrams, herringbone diagrams, cause-and-effect diagrams, or Fishikawa) are causal diagrams created by Kaoru Ishikawa (1968) that show the causes of a specific event. Common uses of the Ishikawa diagram are product design and quality defect prevention to identify potential factors causing an overall effect. Each cause or reason for imperfection is a source of variation. Causes are usually grouped into major categories to identify these sources of variation. The categories typically include [9].

- People (Man): Anyone involved with the process
- Methods: How the process is performed and the specific requirements for doing it, such as policies, procedures, rules, regulations and laws
- Machines: Any equipment, computers, tools, etc. required to accomplish the job
- Materials: Raw materials, parts, pens, paper, etc. used to produce the final product
- Measurements: Data generated from the process that are used to evaluate its quality
- Environment (Milieu): The conditions, such as location, time, temperature, and culture in which the process operates

Figure.5.13. Example 6M-Ishikawa Fishbone (http://www.kodyaz.com/pmp/ishikawa-diagram.aspx).



B. Monte Carlo Simulation, modelling

- What Is Monte Carlo Simulation?
- What do we mean by "simulation?"
- When we use the word simulation, we refer to any analytical method meant to imitate a real-life system, especially when other analyses are too mathematically complex or too difficult to reproduce.
- Without the aid of simulation, a spreadsheet model will only reveal a single outcome, generally the most likely or average scenario. Spreadsheet risk analysis uses both a spreadsheet model and simulation to automatically analysed the effect of varying inputs on outputs of the modelled system.
- One type of spreadsheet simulation is Monte Carlo simulation, which randomly generates values for uncertain variables over and over to simulate a model.

Monte Carlo simulation was named for Monte Carlo, Monaco, where the primary attractions are casinos containing games of chance. Games of chance such as roulette wheels, dice, and slot machines, exhibit random behaviour.

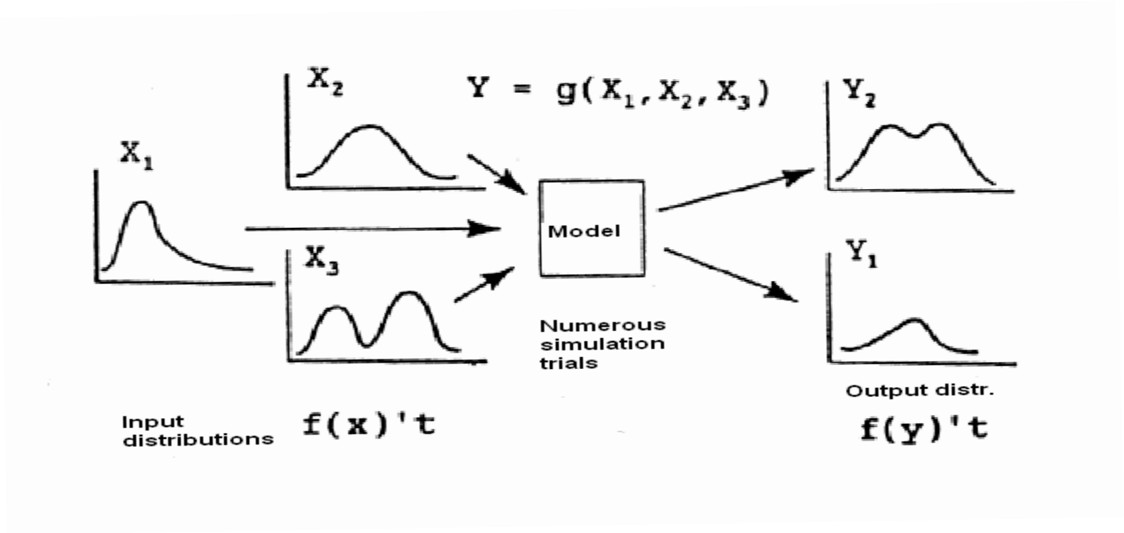
The random behaviour in games of chance is similar to how Monte Carlo simulation selects variable values at random to simulate a model. When you roll a die, you know that either a 1, 2, 3, 4, 5, or 6 will come up, but you don't know which for any particular roll. It's the same with the variables that have a known range of values but an uncertain value for any particular time or event (e.g. interest rates, staffing needs, stock prices, inventory, phone calls per minute) [7].

For each uncertain variable (one that has a range of possible values), you define the possible values with a probability distribution. The type of distribution you select is based on the conditions surrounding that variable. Distribution types include:

To add this sort of function to an Excel spreadsheet, you would need to know the equation that represents this distribution.

A simulation calculates multiple scenarios of a model by repeatedly sampling values from the probability distributions for the uncertain variables and using those values for the cell. Crystal Ball simulations can consist of as many trials (or scenarios) as you want - hundreds or even thousands - in just a few seconds [10].

Figure.5.14. Principle of Monte Carlo simulation.



5.3.5.6. Quantitative accident analysis has the following positive and negative factors

A. Advantages

- Enables the assessment of multiple, co-existing faults and failures
- Functions simultaneously in cases of failure and success
- No need to anticipate end events

- Areas of single point failure, system vulnerability, and low payoff countermeasures may be identified and assessed to deploy resources properly
- paths in a system that lead to a failure can be identified and traced to display ineffective countermeasures.
- Work can be computerized
- Can be performed on various levels of details
- Visual cause and effect relationship
- Relatively easy to learn and execute

Models complex systems into an understandable manner

- Follows fault paths across system boundaries
- Combines hardware, software, environment, and human interaction
- Permits probability assessment
- Commercial software is available

B. Limitations

- Addresses only one initiating event at a time.
- The initiating challenge must be identified by the analyst
- Pathways must be identified by the analyst
- Level of loss for each pathway may not be distinguishable without further analysis
- Success or failure probabilities are difficult to find.
- Can overlook subtle system differences
- Partial successes/failures are not distinguishable
- Requires an analyst with practical training and experience

5.4. Transportation of dangerous goods

ADR (The European Agreement concerning the International Carriage of Dangerous Goods by Road) was done at Geneva 30 September 1957 is entered into force in 29 January 1968. After this first regulations, with a new protocol signed at New York at 21 August 1975 some amendments were done on ADR regulations and these amendments entered into force in 19 April 1985. Last modified version of ADR entered into force in 1 January 2017 [1]. ADR consist of two Annex. ADR regulate the requirements for the classification, packaging, labelling and certification of dangerous goods. It also includes specific vehicle and tank requirements and other operational requirements. Parts of the ADR and related regulations were given in ADR as following:

Annex A: General provisions and provisions concerning dangerous articles and substances (https://www.unece.org/trans/danger/publi/adr/adr_e.html).

Part 1 General provisions

Part 2 Classification

Part 3 Dangerous goods list, special provisions and exemptions related to limited and excepted quantities

Part 4 Packing and tank provisions

Part 5 Consignment procedures

Part 6 Requirements for the construction and testing of packagings, intermediate bulk containers (IBCs), large packagings and tanks

Part 7 Provisions concerning the conditions of carriage, loading, unloading and handling

Annex B: Provisions concerning transport equipment and transport operations

Part 8 Requirements for vehicle crews, equipment, operation and documentation

Part 9 Requirements concerning the construction and approval of vehicles

5.4.1. International carriage of dangerous goods by inland waterways (ADN)

The European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN) was done at Geneva on 26 May 2000 and entered into force on 29 February 2008.

ADN aims the following statements:

- Safety of international carriage of dangerous substances by inland waterways
- Protection of the environment by preventing the possible accident which can be harmful effect on environment
- Facilitating the transportation operation and promote the international trade of dangerous goods [2].

5.4.2. International carriage of dangerous goods by rail (RID)

RID was drawn up by the intergovernmental Organization for International Carriage by Rail (OTIF), comprising 46 member countries. It is established on European territory through European directive 2008/68/EC.RID sets out the safety obligations incumbent upon the shipper and carrier of dangerous goods. Among other headings, these cover [3]:

- safety measures to be taken during loading and unloading of goods the full range of checks to be made prior to wagon departure
- information about the transport itself: the driver must know the contents of the load and the degree of hazard it presents, and wagons must carry information plates stating the nature of the goods and how hazardous they are
- parking and transport conditions
- steps to be taken in the event of accident or incident

5.4.3. Obligations of the main participant of dangerous good transportation

5.4.3.1. Consignor

Consignor is a company which send the dangerous materials to third person or companies. The sender has important tasks to safe delivery of the materials.

- Consignor classifies the dangerous goods and authorize with respect to ADR.
- Consignor should provide the use of right packages given in ADR.
- Consignor should ensure that even empty containers, tanks, vehicles are properly labeled, marked and for the empty tanks they have same degree of leakproffness as if they are full.
- Consignor provides the carrier with necessary transport or accompanying documents like certificates, authorization, approvals, etc.
- Consignor takes services from other participant like loader, filler, packager and that is why consignor should be sure that other participants meet the requirements of ADR, RID or ADN [4-5].

5.4.3.2. Carrier

Carrier is an organization which is undertaking the transportation of dangerous goods. The main task of the carrier is transport and delivery of the materials to third person or organizations. Carrier should responsible from the following duties [5]:

- Secure loading of material to vehicle
- Give information and instruction to driver or carrier about material
- Control the packaging (i.e. Empty or damaged packaging)
- Check the prohibition about the mixed loading of materials
- Road security equipment according to regulation
- Provision of vehicle for loading
- Control that vehicle is not overloading.
- Control of the vehicle, tanks or container for the next test.

5.4.3.3. Loader

- Loader has task about the properly placing of the dangerous material on the carrier [6].
- After secure loading of the material on carrier they should properly mark the vehicle with proper danger marks.
- Beside these tasks they should check the damaged packages or empty packages.
- If mixed loading is exist, loader should provide the proper separation of the materials.

5.4.3.4. Packer

Packer should check requirements concerning packing conditions, mixed packing conditions, package type, preparation of packages for carriage, marking and labelling of the packages [6].

5.4.3.5. Filler

Filler should responsible for the following tasks [6-7]:

- Checking the tanks and its equipment's are in satisfactory conditions before the filling of the material to the tank
- As certain the date of next test for the tank vehicles, battery vehicles, portable tanks etc.
- He shall fill the dangerous goods to appropriate tanks
- He shall fill the tanks up to permissible degree of filling
- He shall check the tanks after the ensure that it is closed and no leakage
- He filler shall ensure that there is no residue of the dangerous material outside of the tank after filling

- He filler should be ensure that orange plates, labels, placards, elevated temperature substances and environmentally hazardous substance prescribed are affixed on the tanks and containers.

5.4.3.5. Unloader

Unloader is responsible with the following tasks [7-8].

- Unloader should be sure that correct materials are unloaded
- Unloader checks that packages, tank, vehicle and container are damaged or not before unloading. If this is the case, unloading will not be carried out until the necessary measures are taken.
- Unloader performs the all procedures about the unloading.
- Following the unloading, unloader should check that all valves are closed and there are no materials adhered to the outside of the tanks or vehicles.

5.4.4. Dangerous goods classification

Dangerous good are classified by ADR as following [9]:

Class 1 Explosive substances and articles

Class 2 Gases

Class 3 Flammable Liquids

Class 4.1 Flammable solids, self-reactive substances and desensitized explosives

Class 4.2 Substances liable to spontaneous combustion

Class 4.3 substances which, in contact with water, emit flammable gases

Class 5.1 Oxidizing substances

Class 5.2 Organic peroxides

Class 6.1 Toxic substances

Class 6.2 Infectious substances

Class7 Radioactive Material

Class 8 Corrosive substances

Class 9 Miscellaneous dangerous substances and articles

Each individual substance or group is given with a unique number known as the ‘’UN’’ number. For example, Petrol is a Class 3 Flammable Liquid and has a unique UN number ‘UN 1203’. Different UN number entries are exists for the naming of dangerous materials.

Following entries types are used for UN number coding [9]:

a) Single entries are used for well-defined substances and substances which contains several isomers for example UN No. of Acetone is 1090 and UN No. of Amyl Acetates (which contains two isomer) is 1104.

b) Generic entries are used for well-defined group of substances for example: UN No: 1133 Adhesives, UN No: 1266 Perfumery Products

c) For certain chemical group or technical nature substances specific entries are used: UN No: 1987 Alcohols, UN No: 1477 Nitrates

d) For the substances which contains one or more dangerous properties general entries are used to cover this group of substances e.g. UN No: 1325 Flammable Solid, Organic

Beside these classifications, materials can be classified with respect to dangerous stage which is given Table 1. [9] This classification can be named as ’’ packacing group ‘’or ‘’ PG’’. For example petroleum is allocated to PG II. In the light of this information transport document of petroleum will be ‘’UN 1203, Petrol, 3, PGII ‘’.

Table.5.14. Classification of materials with respect to dangerous stage [9]

Packaging Group I	High Danger Substances
Packaging Group II	Medium Danger Substances
Packaging Group III	Low Danger Substances (ADR,2015,p97)

Complete lists of UN numbers of dangerous products are given in ADR Chapter 3.2 under Table 2 with the specific material name, class, packaging group, packaging and carriage provisions [10].

Table A contain the following description of the materials [11]:

Column 1: ‘’UN No’’ This column gives the specific UN number of the material. [11]

Column 2: ‘’Name and Description’’ This part is used to give the name of the substance [11]

Column 3a: ‘’Class ‘’ Main class of the material is given in this part [12]

Column 3b: ‘’Classification code‘’ this part covers the sub classification of the dangerous material with respect to ADR 2015 Part 2. [12]

Column 4: ‘’Packing Group’’ Column 4 is contains the information about the appropriate Packing Group of the substance. [12]

Column5: ‘’Labels’’ contains the model number of the labels/placards should be used for the packages, containers, tank-containers, portable tanks and vehicles. (These informations are given in ADR chapter 5) [12]

Column 6: ‘’Specific Provisions’’ gives additional information for example carriage prohibitions, additional labelling. [12]

Column 7a: ‘’Limited Quantities’’ Limitations about the maximum quantity per inner packaging or carrying quantities. [12]

Column 7b:’’Excepted Quantities’’ [13]

Column 8: ‘’Packing Instructions’’ Gives information about packing of dangerous substances [13]

-Alphanumeric codes with R refer to packagings and receptacles (except IBC) or P for the light gauge metal packaging

-Alphanumeric codes starting with ‘’IBC’’ letter refers to Intermediate Bulk Containers

-Alphanumeric codes with ‘’LP’’ refer Large containers.

Column 9a ‘’Specific Packing Provisions’’ gives the specific packing provisions about extra conditions that can be meet. [13]

-Alphanumeric codes starting with ‘’PP’’ or ‘RR’ refer the specific packing provisions for packagings and receptacles

-Alphanumeric number starting with B or BB refers the special packing provisions about IBC’s

-Alphanumeric number starting with ‘’L ‘’ refer special packing provisions for large packagings

Column 9b ‘’Mixed packing provisions’’ Alphanumeric codes starting with the letters ‘’MP’’ [14]

Column 10 ‘’Portable Tank and Bulk Container Instructions’’ [14]

Column 11 ‘’ Portable tank and bulk container specific provisions ‘’ [14]

Column 12 ‘’ Tank codes for ADR ‘’ contains the alphanumeric code which describe the tank type with respect to nature of the materials [14-15]

Column 13 ‘’ Special Provision for ADR tanks ‘’ this part is regulate the extra conditions that can be met. [15]

-Alphanumeric codes starting with ‘’TU’’ gives the special provisions about the use of the tanks

-Alphanumeric codes starting with ‘’TC’’ gives the specific provisions about the construction of the tanks

-Alphanumeric codes starting with ‘’TE’’ gives the specific provisions about the equipment of the tanks

-Alphanumeric codes starting with ‘’TA’’ gives the specific provisions about the approval of the tanks

-Alphanumeric codes starting with ‘’TT’’ gives the specific provisions about the testing of the tanks

-Alphanumeric codes starting with ‘’TM’’ gives the specific provisions about the marking of the tanks

Column14 ‘’Vehicle for tank carriage’’ contains the code of designed vehicle including the drawings of trailers [16].

Column 15 ‘’ Transport Category’’ This part is divided into two part. On the top of the column exemptions related to quantities carried per transport unit and at the bottom of the cell the tunnel restriction code of the substance or article. [16]

Column 16 ‘’Special Provisions for Carriage or Packages ‘’In this column alphanumeric codes starting with V about specific provisions for carriage can be given if it is needed [16].

Column17 ‘‘ Specific provisions for carriage Bulk ‘‘ Contains alphanumeric codes starting with letters ‘’VC’’ as well as the ‘’AP’’ if applicable provisions for carriage in bulk. If there is no code, this means that carriage in bulk is not permitted [16].

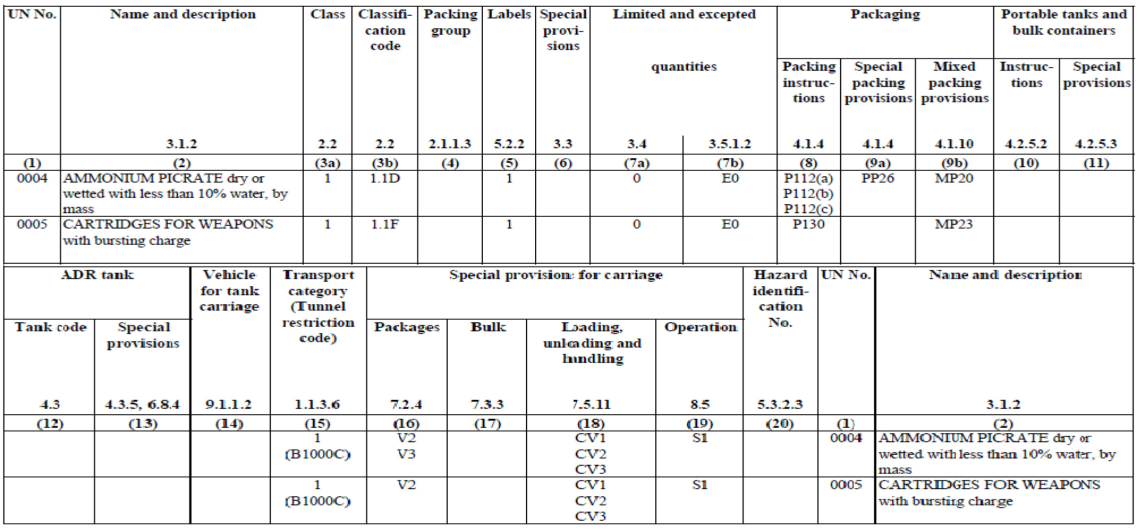
Column 18 ‘‘ Special provisions for carriage – Loading and unloading’’ contains codes starting with CV letters if there is specific instruction for loading, unloading and handling [16].

Column 19 ‘‘ Specific provisions for Carriage-Operation ‘‘ contains numbers staring with ‘’S’’ letter if there is specific provision for operation [16].

Column 20’’ Hazard İdentification Number’’ contains two or three figure number [16].

An example of the Table A part of ADR regulation were given in Figure 5.15.

Figure.5.15. An example of table A [17-18].



UN No.	Name and description	Class	Classification code	Packing group	Labels	Special provisions	Limited and excepted quantities		Packaging			Portable tanks and bulk containers	
									Packing instructions	Special packing provisions	Mixed packing provisions	Instructions	Special provisions
	3.1.2	2.2	2.2	2.1.1.3	5.2.2	3.3	3.4	3.5.1.2	4.1.4	4.1.4	4.1.10	4.2.5.2	4.2.5.3
(1)	(2)	(3a)	(3b)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9a)	(9b)	(10)	(11)
0004	AMMONIUM PICRATE dry or wetted with less than 10% water, by mass	1	1.1D		1		0	E0	P112(a) P112(b) P112(c)	PP26	MP20		
0005	CARTRIDGES FOR WEAPONS with bursting charge	1	1.1F		1		0	E0	P130		MP23		

ADR tank		Vehicle for tank carriage	Transport category (Tunnel restriction code)	Special provision for carriage				Hazard identification No.	UN No.	Name and description
Tank code	Special provisions			Packages	Bulk	Loading, unloading and handling	Operation			
4.3	4.3.5, 6.8.4	9.1.1.2	1.1.3.6	7.2.4	7.3.3	7.5.11	8.5	5.3.2.3		3.1.2
(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(1)	(2)
			1 (B1000C)	V2 V3		CV1 CV2 CV3	S1		0004	AMMONIUM PICRATE dry or wetted with less than 10% water, by mass
			1 (B1000C)	V2		CV1 CV2 CV3	S1		0005	CARTRIDGES FOR WEAPONS with bursting charge

5.4.5. Packaging, marking and hazard labelling

5.4.5.1. Use of overpacks

If an overpack is used it should be marked with the word ‘’OVERPACK’’ which should be minimum 12 mm high, UN Number and enviromentally hazardous substance mark if it is required. Additionally, to these markings orientation arrows is also used on two opposite side of overpacks [19].

5.4.5.2. Empty uncleaned packagings, tanks, MEMUs, vehicles and containers in bulk

Empty uncleaned packagings, tanks, tank containers, MEMUs, vehicles and containers in bulk should be labelled as if they are full. Containers used for the carriage of radioactive materials should not be used for the carriage of other substance if they arent contaminated below the radioactivity level of 0.4 Bq/cm2 for beta and gamma emitters, low toxicity alpha emitters and 0.04 Bq/cm2 for other alpha emitters [19].

5.4.5.3. Mixed packing

If there are two different dangerous materials are packed in same outer package, the package should be labelled and marked for each substance. Only one label is used on the package if two the material is required the same label [20].

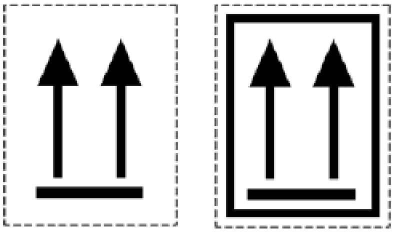
5.4.5.4. Marking and labelling (ADR 2015 Vol 2, page 217)

Package is marked with UN number of the dangerous good with ‘’UN’’ letter. All package markings must be visible and legible. Salvage packaging shall be marked with the Word ‘’ SALVAGE’’ additionally. Beside this Intermediate Bulk Containers contains more than 450 liters capacity must be marked on two opposite sites [21]. For the environmentally hazardous substance following mark with the given dimensions shall be on packageFigure 5.16.

Figure.5.16. Dimension of environmentally hazardous substance marks dimensions [22].

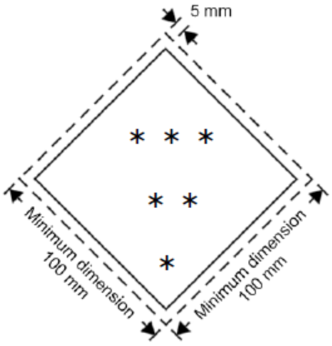
Orientation of the package is also important parameter for the transportation of the package and this information is also given on the package with one of the following marks [23] (Figure 5.17).

Figure.5.17. Orientation of the package [23].



Labelling of the package to describe the which type of hazardous material exist in package can inform by using the special marks. Each class of dangerous materials has its own mark. The size of the diamond shape class label is given below [24].

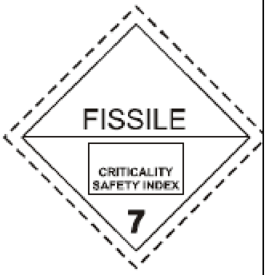
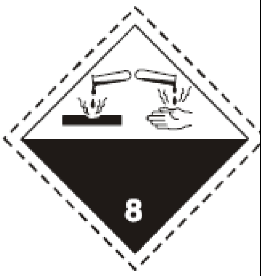
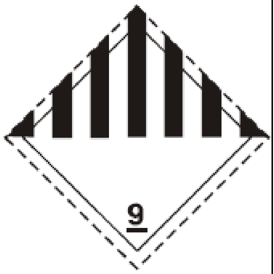
Figure.5.18. Dimension of dangerous material marks on the package [24].



The detailed hazardous materials labels were given in Figure.5.19 [25-26-27].

Figure.5.19. Structure of dangerous material labels [25-26-27].

			
Explosive substances or articles	Flammable Gases	Flammable Gases	Nonflammable, non-toxic gases
			
Nonflammable, non-toxic gases	Toxic gases	Flammable Liquids	Flammable Liquids

			
Flammable solids, self-reactive substances and solid desentized explosives	Substances liable to spontaneous combustion	Substances which, in contact with water, emit flammable gases	Substances which, in contact with water, emit flammable gases
			
Oxidizing Substance	Organic Peroxides	Organic Peroxides	Toxic Substances
			
Infectious Substance	Radioactive Material Category I	Radioactive Material Category II	Radioactive Material Category III
			
Radioactive Material – Fissile Material	Corrosive Substances	Miscellaneous dangerous substances and articles	

5.4.5.5. Requirements for the construction and testing of packagings

Construction and Testing of the Packaging Materials are regulates by the ADR chapter 6.1 [28]. ADR, ADN and RID is also regulate the correct way of the packaging of the materials in box, drum, container or tanker. In most cases packaging is UN approved. This means that package has been tested and approved according to ADR, ADN and RID. An example of UN approved packaging code was given in Figure 5.20.

Figure.5.20. Packaging Code on a Package [29].

Package codes with respect to designation type consists of following parts [30]:

i) An Arabic number identify the kind of the package for example bag, box. If the package is composite materials two letters can be used. First letter is used for inner receptable and the second is for outer package.

To identicate the kinds of packagings following numbers can be used (Table 5.15).

Table.5.15. Kinds of Packaging.

1	Drum
2	(Reserved)
3	Jerrican
4	Box
5	Bag
6	Composite Packaging
7	(Reserved)
0	Light gauge metal packagings

ii)A capital letter(s) gives information about the package material. Following letters are used for different kinds of packaging materials (Table 5.16):

Table.5.16. Kinds of packaging material.

A	Steel (All types including surface treated)
B	Aluminium
C	Natural Wood
D	Plywood
F	Reconstitıted wood
G	Fibreboard
H	Plastic Material
L	Textile
M	Paper, multiwall
N	Metal (other than steel or Aluminium)
P	Glass, porcelain or stonewear

iii)Third number indicates the category of packaging material [30].

In table 5.17, an example from some examples were given about the coding of package material. Detailed table about the coding of package materials are given in ADR 2015 Volume 2, pages 269-270.

Table 5.17. Some examples about the coding of package material.

Kind	**Material**	**Category**	**Code**
Jerrican	Aluminium	Non-removable head	3B1
Boxes	Plastic	Solid	4H2
Drums	Steel	Removable head	1A2
Bags	Textile	Water Resistant	5L3

Marking of the packages contain the following informations [31]:

1.a)The United Union Packaging Symbol un : This symbol shows that this package is certified with UN standards[31].

1.b) The symbol ‘’RID/ADR’’ for composite packagings and light gauge metal packaging conforming the certification of the package [31].

2. The code of Packaging: This code gives information about the package materials described in Part X for examle 4B2 refer the Solid Plastic Boxes [31].

3. In this part code is consist of two parts. First part is gives which packing group materials can be packaged with this package material. X, Y or Z symbols are used to categorize this part as given below [31].

Table.5.18. Packing group symbols.

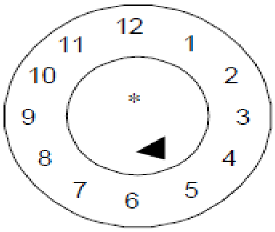
X	Packing Group I,II, III
Y	Packing Group II, III
Z	Packing Group III

Second part of the code gives the relative density for example Y1.4 means this package is proper for Packing Group II, III and relative density is 1.4. If the relative density of the material doesn’t exceed the 1.2 it is not applicable. If package intended to contain solid or with inner packaging, the maximum gross mass in kg should be written.

4.’’S’’ letter is used for the packaging intended to carriage of solids or inner packaging, or packaging designed to carry liquid material. ‘’S’’ letter is also used for the light gauge metal packagings to carry liquid materials [32].

5. The last two digit of the manufacturing year should be given. This part is given in a different place of the package as given in below: Month is showed with an arrow in the middle point of the mark as last two digit of the manufacturing year is written [32].

Figure.5.21. Manufacturing date example.



6. The name of the country which is allocated the mark to distinguish the vehicle in international traffic [32].

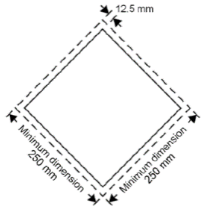
7. The name of the manufacturer or other identification of the package specified by the authority should be added lastly [32].

When selecting the correct package type, care must be taken to ensure the “packing instruction” in ADR is followed and the package is suitable for the dangerous goods. The various packaging instructions for individual UN numbers are provided in the ADR Dangerous Goods List (Chapter 3, Table A, Column 8).

5.4.6. Placarding and marking of containers, tanks containers, portable tanks and vehicles

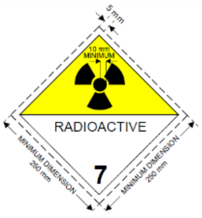
Containers, MEGCs, tank containers and portable tanks should be placarded on each side and end of the container or tank. If the tank container or portable tank has two compartment or carries two or more dangerous good placard should be applied on each side of the relevant container and placard of each substance at the both ends of the container. If these placards aren’t visible from outside of the vehicle, same placards should be affixed on same sides of the vehicle if the placards are visible no need to extra placarding on the vehicle. [33-34]. Dimensions of the standard placard for vehicle or containers were given in Figure 5.22 except for Class 7.

Figure.5.22. Dimension of standard placard for vehicle [35].



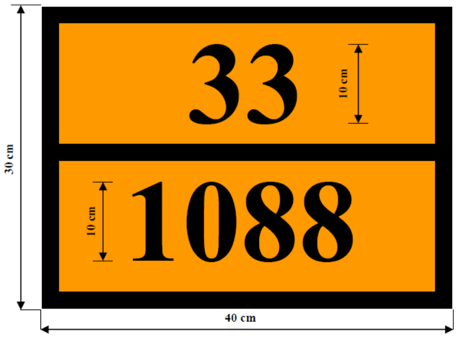
Dimension and structure of the Class 7 radioactive material placard was given in Figure 5.23.

Figure.5.23. Dimension and structure of Class 7 materials placard for vehicle [36].



Beside the hazardous materials identification placard vehicles which carry hazardous substances should be marked with orange colored plate on the rear sides (Figure 5.24.). This plate consists of two rectangular orange plates. The dimension of orange plate is 40 cm wide and 30 cm height and with the black borders 15 mm wide. The number given in the plate should have the 10 cm height [37].

Figure.5.24. Structure and dimension of orange plate placard [38].



The hazard identification is given on the first row on the oranges plate. Another important information is given on the second row of the orange plate is UN number of the hazardous material. UN number is given as four figures [38]. Hazard identification number is consist of two or three figures. General hazards are given with the following numbers.

2 Emission of gas due to pressure or to chemical reaction

3 Flammability of liquids and gases or self-heating liquid

4 Flammability of solids or self-heating solids

5 Oxidizing effect

6 Toxicity or risk of infection

7 Radioactivity

8 Corrosivity

9 Risk of spontaneous violent reaction

When hazards can be indicated with a single number of the given above, the number is followed by zero. Combination of figures for example 22, 44, 446 have special meanings. Beside this if the number has X term, this means that substance gives reaction dangerously with water. Some examples of hazard identification were given below [39-40-41].

20 inert gas

22 refrigerated gas

223 refrigerated flammable gas

225 refrigerated oxidizing (fire-intensifying) gas

23 flammable gas

236 flammable gas, toxic

239 flammable gas, which can spontaneously lead to violent reaction

25 oxidizing (fire-intensifying) gas

26 toxic gas

265 toxic gas, oxidizing (fire-intensifying)

266 highly toxic gas

268 toxic gas, corrosive

286 corrosive gas, toxic

30 flammable liquid or self-heating liquid

323 flammable liquid which reacts with water emitting flammable gases

X323 flammable liquid which reacts dangerously with water emitting flammable gases

33 highly flammable liquid (flash point below 21°C)

333 pyrophoric liquid

X333 pyrophoric liquid which reacts dangerously with water

336 highly flammable liquid, toxic

338 highly flammable liquid, corrosive

X338 highly flammable liquid, corrosive, which reacts dangerously with water

339 highly flammable liquid, which can spontaneously lead to violent reaction

36 self-heating liquid, toxic

362 flammable liquid, toxic

X362 flammable liquid, toxic, which reacts dangerously with water emitting flammable gases

38 self-heating liquid, corrosive

382 flammable liquid, corrosive, which reacts with water emitting flammable gases

X382 flammable liquid, corrosive, which reacts dangerously with water emitting flammable gases

39 flammable liquid, which can spontaneously lead to violent reaction

40 flammable self-heating solid

423 solid, which reacts with water emitting flammable gases

X423 flammable solid, which reacts dangerously with water emitting flammable gases

44 flammable solid, in molten state, at elevated temperature

446 flammable solid, toxic, in molten state, at elevated temperature

46 flammable or self-heating solid, toxic

462 toxic solid, which reacts with water emitting flammable gases

48 flammable or self-heating solid, corrosive

482 corrosive solid, which reacts with water emitting flammable gases

50 oxidizing (fire-intensifying) substance

539 flammable organic peroxide

55 strongly oxidizing substance

556 strongly oxidizing substance, toxic

558 strongly oxidizing substance, corrosive

559 strongly oxidizing substance, which can spontaneously lead to violent reaction

56 oxidizing substance, toxic

568 oxidizing substance, toxic, corrosive

58 oxidizing substance, corrosive

59 oxidizing substance which can spontaneously lead to violent reaction

60 toxic or harmful substance

63 toxic or harmful substance, flammable (flash point between 21°C and 55°C)

638 toxic or harmful substance, flammable (flash point between 21°C and 55°C), corrosive

639 toxic or harmful substance, flammable (flash point between 21°C and 55°C), which can spontaneously lead to violent reaction

66 highly toxic substance

663 highly toxic substance (flash point not above 55°C)

68 toxic or harmful substance, corrosive

69 toxic or harmful substance, which can spontaneously lead to violent reaction

70 radioactive material

72 radioactive gas

723 radioactive gas, flammable

73 radioactive liquid, flammable (flash point not above 55°C)

74 radioactive solid, flammable

75 radioactive material, oxidizing

76 radioactive material, toxic

78 radioactive material, corrosive

80 corrosive or slightly corrosive substance

X80 corrosive or slightly corrosive substance, which reacts dangerously with water

83 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C)

X83 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which reacts dangerously with water

839 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which can spontaneously lead to violent reaction

X839 corrosive or slightly corrosive substance, flammable (fp between 21°C and 55°C), which can spontaneously lead to violent reaction and which reacts dangerously with water

85 corrosive or slightly corrosive substance, oxidizing (fire-intensifying)

856 corrosive or slightly corrosive substance, oxidizing (fire-intensifying) and toxic

86 corrosive or slightly corrosive substance, toxic

88 highly corrosive substance

X88 highly corrosive substance, which reacts dangerously with water

883 highly corrosive substance, flammable (flash point between 21°C and 55°C)

885 highly corrosive substance, oxidizing (fire-intensifying)

886 highly corrosive substance, toxic

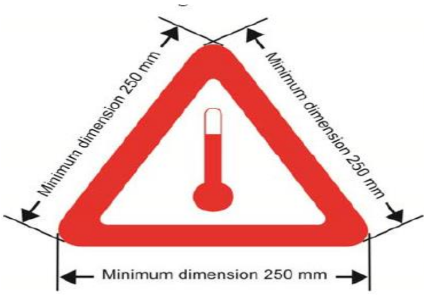
X886 highly corrosive substance, toxic, which reacts dangerously with water

89 corrosive or slightly corrosive substance, which can spontaneously lead to violent reaction

90 miscellaneous dangerous substance

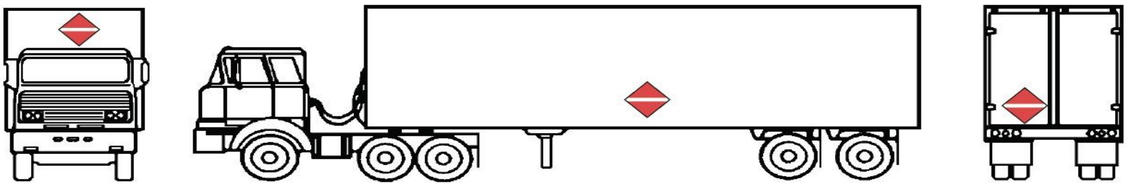
Tanks-vehicles, tank containers, portable tanks, special vehicles which carry materials like liquid state above 100°C or solid materials above 240°C should be marked with the mark given in Figure 5.25. This mark shall bear on both sides and rear sides of the vehicle and on both sides and back side of the tank container, portable tank [41].

Figure.5.25. Mark for the carriage of substance at elevated temperatures [41].



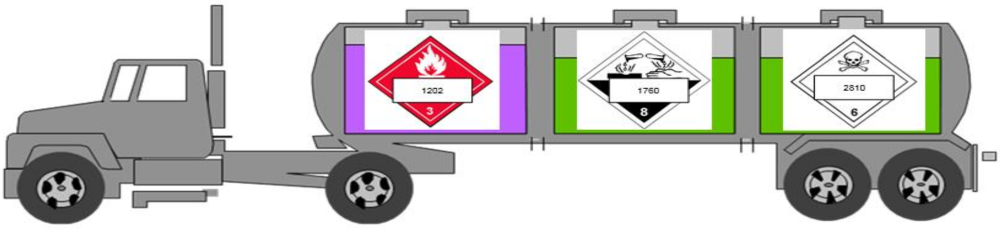
Placarding is important aspect of safety transportation of dangerous goods. Placarding of the vehicle or containers provide the identification of dangerous materials. Placards should be affixed to both sides and both ends of the tank or container (Figure 5.26) [33].

Figure.5.26. Marking of vehicles with dangerous materials placards [42].



If the tanks or container consist of more than one comportment and carries two or more dangerous materials, appropriate placard affixed along each side on the related compartment and shown ends as given in Figure 5.27 [34].

Figure.5.27. Placarding of vehicles which contains more than one dangerous goods [43].



For the vehicles containing Class 1 substance packages or radioactive materials, relevant placard should be affixed on each side and rear of the vehicle.

If the relevant placards markings are not visible from outside of the carrying vehicles, same placards shall be fixed on each side and both ends of the vehicle.

Orange colored plate which contains hazard identification number and UN number shall be affixed on front and rear part of the vehicle (Figure 5.28).

Figure.5.28. Orange plate marking of vehicles [44].

During the carriage of dangerous goods in tanks, ADR requires marking of both the vehicle and tank. In this case numbered orange plates at the front and rear of the vehicle, hazard placards and other marks as required on each side of the tank and at the rear (Figure 5.29).

Figure.5.29. Placarding of tanks [45].

5.4.7. Requirements for the training of vehicle crew [46-47]

Driver should have the certificate which is given by the authority after passing the exam at the end of a special training courses. This causes should include the following subjects:

- Type of hazards
- General information about the requirements about carriage of dangerous goods
- Restrictions about traffic for example tunnel restrictions
- Rules about mixed loading in same package or in same vehicle
- Things should do or shouldn’t do during the transportation
- Appropriate marking, placarding, labelling
- Basic information what to do in case of accident
- Technical equipment which is needed
- Specific requirements for the vehicles
- Hazards can be faced after an explosion
- Hazards which is related with ionization radiation

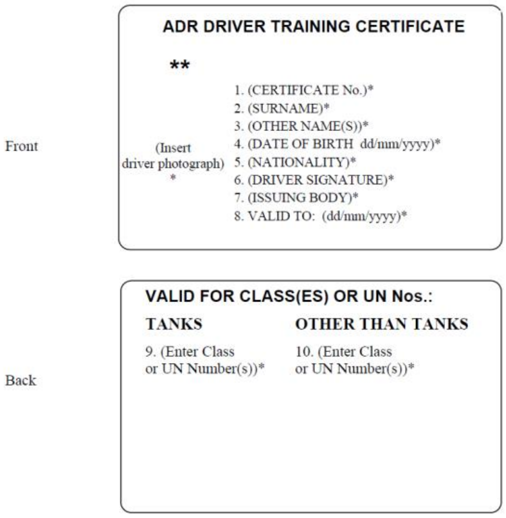
Minimum training programme is including the following parts:

- Basic training: 18 teaching units
- Training for carriage in tanks: 12 training units
- Training for the specialization of the Class I materials: 8 teaching units

- Specific training for the carriage of the Class 7 radioactive materials: 8 teaching units

A driving certificate is valid for five years. The driver certificate is made from white plastic card and black lettering on it. The information on the driving certificate is given with the one of languages used in the country. If the one of these used languages is not German, French or English, all titles should be given also in English, German or French. A sample driving certificate was given in the following figure [48].

Figure.5.30. Driving certificate [48].



Front

ADR DRIVER TRAINING CERTIFICATE

**

(Insert
driver photograph)
*

1. (CERTIFICATE No.)*
2. (SURNAME)*
3. (OTHER NAME(S))*
4. (DATE OF BIRTH dd/mm/yyyy)*
5. (NATIONALITY)*
6. (DRIVER SIGNATURE)*
7. (ISSUING BODY)*
8. VALID TO: (dd/mm/yyyy)*

Back

VALID FOR CLASS(ES) OR UN Nos.:

TANKS	OTHER THAN TANKS
9. (Enter Class or UN Number(s))*	10. (Enter Class or UN Number(s))*

5.4.8. Miscallenous equipment and personal protection equipment’s

Each transport unit must be equipped with items for personal protection or general purpose. The following items shall be exist on board during transportation [49-50].

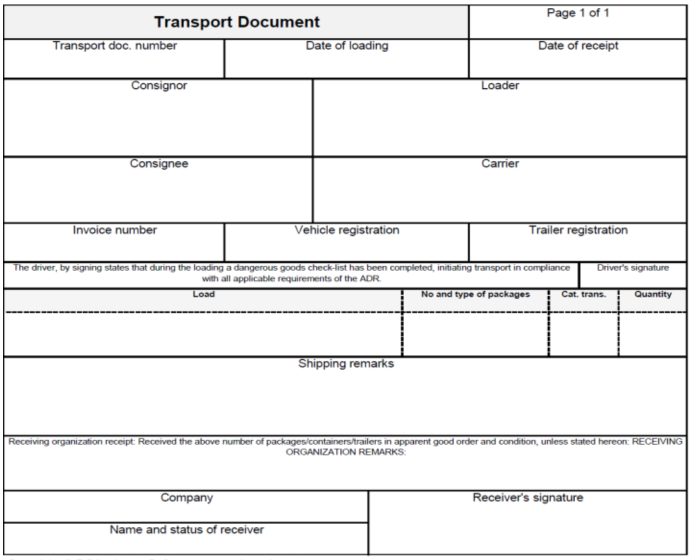
- A Wheel chock which has suitable size with respect to the diameter and maximum mass which will be applied to chock.
- Two self-standing warning signs.
- Eye rinsing liquid.
- Eye protection goggles.
- Protective gloves.
- Portable lightning apparatus
- A warning vest

5.4.9. Documentation

Documentation is an important aspect of the transportation of dangerous goods safetly. Following documents must be carried on the transportation unit [51]:

- The transport document detailing all the dangerous goods carried;

Figure.5.31. ADR transport document [52].



Transport Document

Page 1 of 1

Transport doc. number

Date of loading

Date of receipt

Consignor

Loader

Consignee

Carrier

Invoice number

Vehicle registration

Trailer registration

The driver, by signing states that during the loading a dangerous goods check-list has been completed, initiating transport in compliance with all applicable requirements of the ADR.

Driver's signature

Load	No and type of packages	Cat. trans.	Quantity

Shipping remarks

Receiving organization receipt: Received the above number of packages/containers/trailers in apparent good order and condition, unless stated hereon: RECEIVING ORGANIZATION REMARKS:

Company

Name and status of receiver

Receiver's signature

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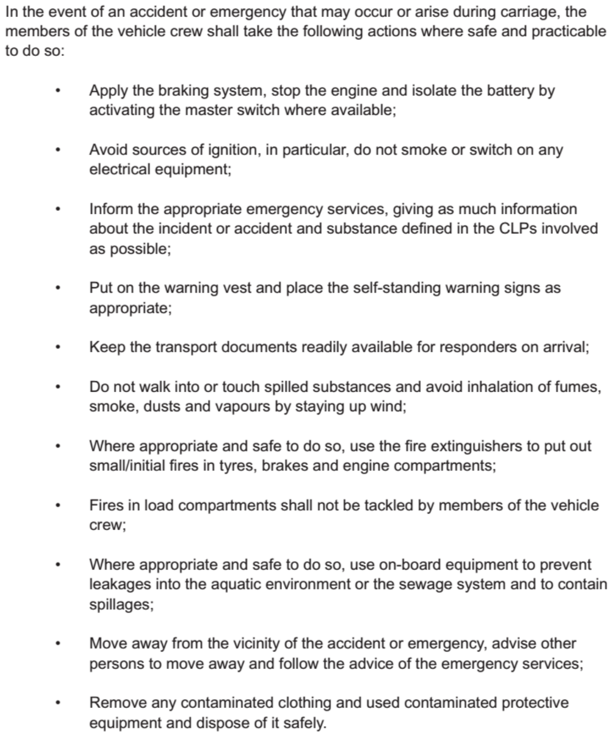
- The writing instructions given to the crew or driver what should be done during emergency.

Figure.5.32. An example of writing instructions [53].



In the event of an accident or emergency that may occur or arise during carriage, the members of the vehicle crew shall take the following actions where safe and practicable to do so:

- Apply the braking system, stop the engine and isolate the battery by activating the master switch where available;
- Avoid sources of ignition, in particular, do not smoke or switch on any electrical equipment;
- Inform the appropriate emergency services, giving as much information about the incident or accident and substance defined in the CLPs involved as possible;
- Put on the warning vest and place the self-standing warning signs as appropriate;
- Keep the transport documents readily available for responders on arrival;
- Do not walk into or touch spilled substances and avoid inhalation of fumes, smoke, dusts and vapours by staying up wind;
- Where appropriate and safe to do so, use the fire extinguishers to put out small/initial fires in tyres, brakes and engine compartments;
- Fires in load compartments shall not be tackled by members of the vehicle crew;
- Where appropriate and safe to do so, use on-board equipment to prevent leakages into the aquatic environment or the sewage system and to contain spillages;
- Move away from the vicinity of the accident or emergency, advise other persons to move away and follow the advice of the emergency services;
- Remove any contaminated clothing and used contaminated protective equipment and dispose of it safely.

- Identification cards of the each vehicle crew including a photograph of the crew.
- Drivers training certificate
- When appropriate, the large container or vehicle packing certificate;
- The annual vehicle certificate of approval
- A copy of authority approval

Exercises Questions for Chapter 5.1, 5.2 and 5.3

1. BLEVE refers to accidents with toxic gases

a) yes

b) no

2. LD50 is a measure of chronic toxicity

a) yes

b) no

3. LPG includes gas in liquid form

a) yes

b) no

4. Detonation causes a shock wave

a) yes

b) no

5. Duration of a dynamic accident is much longer than that of static accident

a) yes

b) no

6. Lethal concentration of toxic gas leaks can reach to few kilometres' distance

a) yes

b) no

7. Flammability risk of LPG cloud cannot reach to the distance of few kilometres

a) yes

b) no

8. If gas leaks in liquid form, it causes a longer danger area than if it leaks in gas form

a) yes

b) no

9. In BLEVE explosion of LPG tank missiles can fly up to few kilometres

a) yes

b) no

10. Most common chemicals in transportation accidents are corrosives (ADR 8)

a) yes

b) no

11. In case of a rupture of a normal LPG bottle (11 kg) the 3rd degree burns can be obtained at over ten meters' distance

a) yes

b) no

12. Humans can stand an overpressure of 50 kPa without injuries

a) yes

b) no

13. Ammonia is less dangerous than chlorine

a) yes

b) no

14. Radiation dose of 3 Sievert can be lethal

a) yes

b) no

15. Fire water (extinguishing water) from fires of toxics can cause environmental accident in water course.

a) yes

b) no

16. Expert analysis uses the principle of causality to determine the course of events

a) yes

b) no

17. FMEA and FMECA should be applied as soon as system design information is available

a) yes

b) no

18. Detection rate (D) of FMEA is high, when the system is under control

a) yes

b) no

19. The lowest level of Accimap diagram represents legislative control

a) yes

b) no

20. Top event of fault tree diagram is the final accident itself

a) yes

b) no

21. Fault tree continues visually from the end of event tree

a) yes

b) no

22. Result of Boolean logic 0,5 AND 0,5 OR 0,5 is 0,75

a) yes

b) no

23. It is recommended to calculate probabilities of event tree elements by fault tree

a) yes

b) no

24. By Fishbone analysis you can find out the root causes of an accident

a) yes

b) no

25. Normal distribution is the most easiest distribution on probability calculations

a) yes

b) no

26. Tools for risk identification are not

a) stuff reaction matrix

b) process charts

c) interviews

d)modelling

e) brain storming

27. Silent brain storming as risk identification is a suitable tool, because

a) it’s fast

b) it’s independent

c) there is no underrating by others

d) it’s easy to arrange

e) good findings are guaranteed

28. Process orientation of risk identification means, that

a) the risks of each process are identified separately at a time

b) all processes can have severe risks

c) process staff (owners) identifies the risks

d) all processes have different risks

e) the risk management activities can be targeted to the right processes

29. Probability of the risk cannot be indicated by

a) range 0 - 1

b) range 0 – 100 %

c) time frequency

d) determined values 1,2,3,4,5

e) value in €

30. Consequence of the risk cannot be indicated by

a) number of injured persons

b) velocity of stuff movement

c) value in €

d) volume

e) area

31. Computer models can be used for

a) estimation of probabilities

b) estimation of accident costs

c) stuff movement

d) stuff transforms

e) decision support

32. Monte Carlo analysis not

a) is a risk analysis tool

b) gives exact emission values as output

c) bases on calculation models

d) is basically only an algorithm

e) needs input data as distributions

33. Event tree

a) is not an accident analyses tool

b) describes the events before accidents

c) describes the events after accident

d) is basing on dependent probabilities

e) needs knowledge about protection activities

34. Fault tree not

a) includes top accident

b) includes initial events

c) includes links between events

d) includes responsibilities

e) deals with logic operators

35. Hazop

a) is only applied on process planning

b) can be used as accident analysis tool

c) contains so called guide words

d) is a graphical method

e) results are collected on table

36. According to Bayesian logic and operating with probabilities

a) “AND” means addition

b) “AND” means average

c) OR” means addition

d) “OR” means multiplication

e) “OR” > “AND”

37. FMEA

a) Starts from process identification

b) does not take probabilities into account

c) contains estimations of accident consequences

d) includes not management activities

e) includes effect analyses of improvement activities

Answers for Chapter 5.1, 5.2 and 5.3

1. No
2. Yes
3. Yes
4. Yes
5. No
6. Yes
7. No
8. Yes
9. Yes
10. No
11. Yes
12. Yes
13. Yes
14. No
15. Yes
16. No
17. Yes
18. Yes
19. No
20. Yes
21. No
22. Yes
23. Yes
24. Yes
25. Yes
26. D
27. C
28. A, C and E
29. E
30. B
31. A, C, D and E
32. B
33.C, D and E
34. D
35. B, C and E
36. C and E
37. A, C, and E

Exercises Questions for Chapter 5.4

1. Which of the following is not a personel protection equipment?

a) Eye protection googles

b) Protective gloves

c) Eye rinsing liquid

d) Wheel chock

2. Which of the following regulates the transportation of dangerous goods by road?

a) ADN

b) RID

c) ADR

d) IATA

3. …………. regulates the transport of dangerous goods by railway. Complete the sentence.

a) ADR

b) ADN

c) IATA

d) RID

4. Which of the following is not a document needed during transportation?

a) Driving Certificate

b) Authority Approval

c) Transport Document

d) Safety Data Sheet

5. Which of the following is not a part of Table A give in ADR?

a) UN Number

b) Name and Description of Material

c) Packaging Group

d)Marking of vehicle

6. What means the following Figure?

a) Over pack

b) Carriage of substance at elevated temperature

c) Orientation of package

7. Orange plates placard consist of two different parts.

a) True

b) False

8. First row of orange plate placards gives the hazard identification number.

a) True

b) False

9. UN number is given in four digits.

a) True

b) False

10. Radioactive hazard number is given by 7?

a) True

b) False

11. Standard hazard placard has diamond structure with dimensions 250 mmx250 mm?

a) True

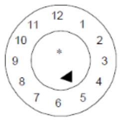
b) False

12. ‘’S’’ letter on a package is used for the light gauge metal packagings to carry liquid materials?

a) True

b) False

13. What means the following Figure?



a) Production date of the packaging

b) Material code of the material

c) Code of the package type

14) P letter on package means that package material is ……………….

a) Textile

b) Paper

c) Plastic

d) Metal

15. 3 number on a package denotes which kind of package?

a) Drum

b) Box

c) Bag

d) Jerrican

16. What means the following dangerous good label?

a) Flammable Gases

b) Radioactive Materials

c) Organic Peroxides

d) Infectious Substances

17. What means the following dangerous good label?

a) Environmentally dangerous substance

b) Orientation of Package

c) Organic peroxides

d) Radioactive Material

18. Which of the following is not one of the task of carrier?

A) Control that vehicle is not overloading

b) Control of the vehicle, tanks or container for the next test

c) Secure loading of material to vehicle

d) Preparation of transport documents

19. Which of the following is not true?

a) Loader should check the properly seperation of the materials if mixed loading is existing

b) Filler shall fill the dangerous goods to appropriate tanks

c) Consignor should provide the use of right packages given in ADR

d) Provision of vehicle for loading provided by consignor

20. 23 Hazard number means which of the following?

a) Flammable Gas

b) Toxic Gas

c) Highly Flammable Liquid

d) Strongly Oxidizing Substance

Answers for Chapter 5.4

1. D
2. C
3. D
4. D
5. D
6. B
7. A
8. A
9. A
10. A
11. A
12. A
13. A
14. E
15. C
16. D
17. A
18. D
19. D
20. A

CHAPTER 6

IMPLEMENTATIONS

6.1. Case study (TURKEY)

6.1.1. Scope of study

The book which is about “the forming the competency based education modules for chemical accident prevention, preparedness and response”, section 2.2.1 CLP regulation; is given methods of theclassification a chemical substance/mixtures. In this case study, the crude benzol will be examined in terms of physical, health and environmental hazards. A safety data sheet will be created by performing a crude benzol classification work in this study. A SDS form consist of 16 subtitles (given Annex-/SDS format) but in this study, relating to the classification; section 2 will be examined.

6.1.1.1. Creation of crude benzol SDS

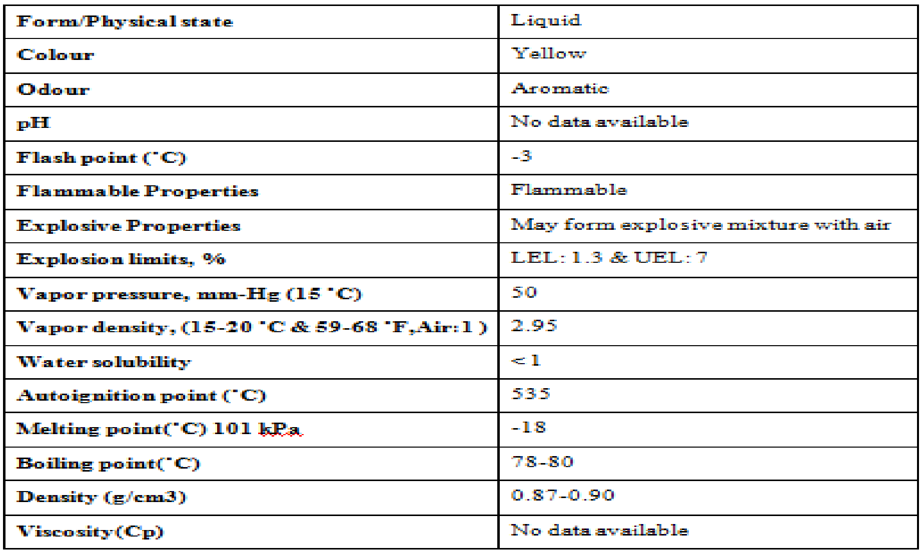
A. How and where get the general information of mixture?

Usually; this information of substances/mixtures are received from manufacturer or determined are given at section 4.2.2.1 physical test methods.

For Classifying of a chemical substance/mixture; the least information about the physical, chemical properties and content information at figure 1-2 should know.

For crude benzol; the appearance, physical and chemical properties and content information; received from the manufacturer is as follows.

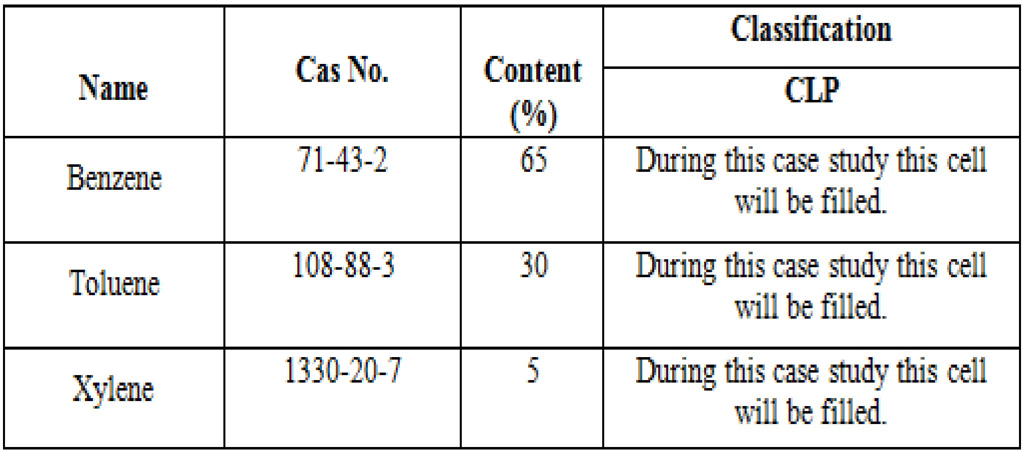
Figure.6.1. Physical and chemical properties of mixture.



Form/Physical state	Liquid
Colour	Yellow
Odour	Aromatic
pH	No data available
Flash point (˚C)	-3
Flammable Properties	Flammable
Explosive Properties	May form explosive mixture with air
Explosion limits, %	LEL: 1.3 & UEL: 7
Vapor pressure, mm-Hg (15 ˚C)	50
Vapor density, (15-20 ˚C & 59-68 ˚F,Air:1)	2.95
Water solubility	< 1
Autoignition point (˚C)	535
Melting point(˚C) 101 kPa	-18
Boiling point(˚C)	78-80
Density (g/cm3)	0.87-0.90
Viscosity(Cp)	No data available

The content information is received from manufacturer as follows and Crude benzol is a mixture of; benzene, toluene, Xylene.

Figure. 6.2. The content of mixture.



Name	Cas No.	Content (%)	Classification
			CLP
Benzene	71-43-2	65	During this case study this cell will be filled.
Toluene	108-88-3	30	During this case study this cell will be filled.
Xylene	1330-20-7	5	During this case study this cell will be filled.

B. How do we classification of crude benzol or any mixture?

Classification of any hazardous substance or mixture; given methods of the classification at section CLP regulation are performed.

In this study, it was given how to obtain the information of chemicals in order to be able to classify hazardous substance or mixture. Also, classification information of substance in the mixture; can be obtained by using CAS. No., EC. No., etc. of registered substance from web sites below.

- https://echa.europa.eu/
- http://gestis-en.itrust.de/nxt/gateway.dll/gestis_en/000000.xml?f=templates$fn=default.htm$vid=gestiseng:sdbeng$3.0

In this case study, the classification informations of substances in the mixture; By using CAS no. and EC no. Informations of substances which content informations are given figure 2, was obtained from the sites specified above and make calculation.

6.1.1.2. How to access registered chemical information?

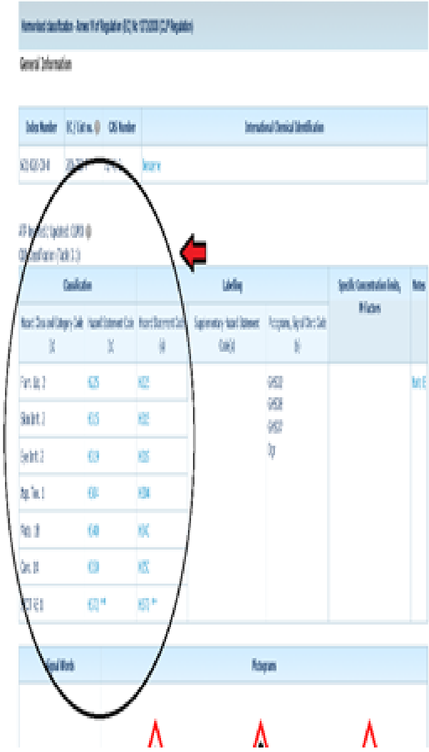
The following steps are followed.

1.Use the web ste: https://echa.europa.eu/ and write the cas registry no. or EC number of components.

2.For each component of forming the mixture; the Substance information form use.

3.For each component of forming the mixture; C&L inventory at the Substance information form use.

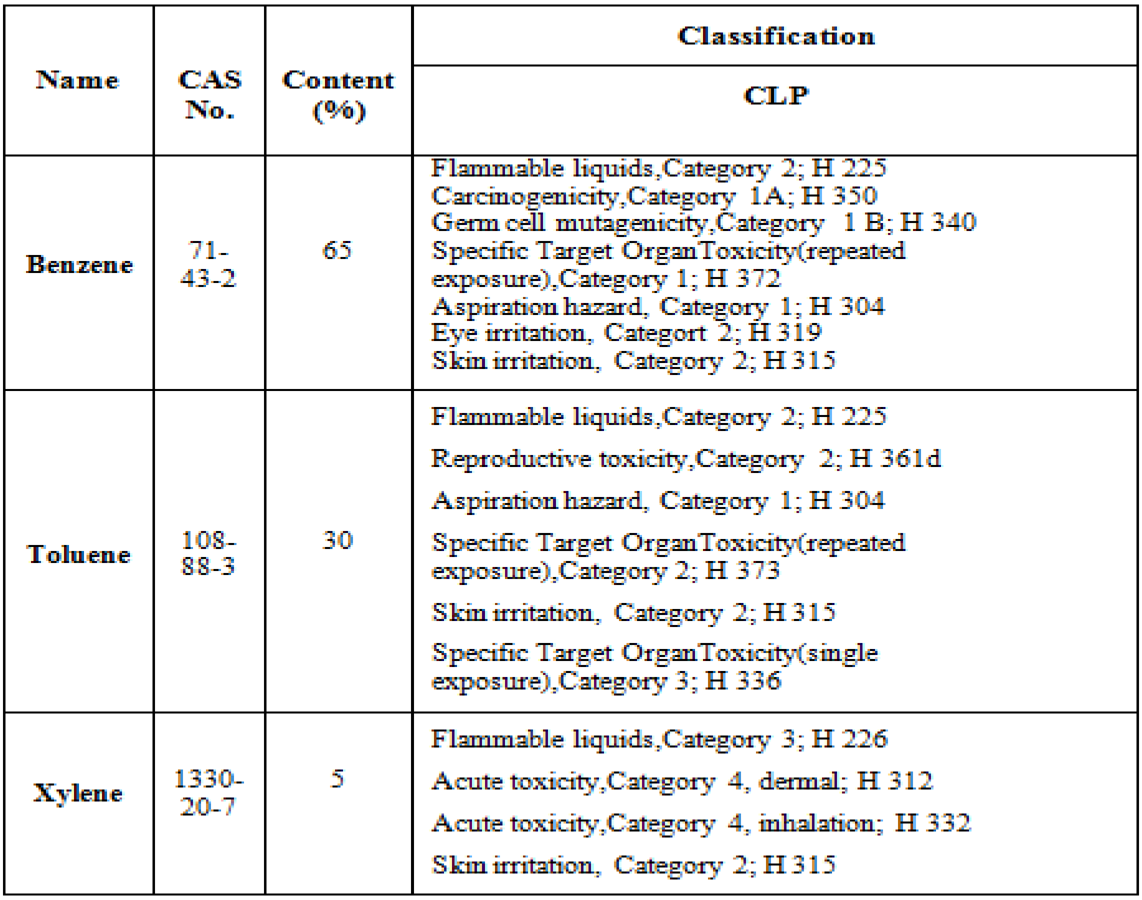
4. For each component of forming the mixture; Get the classification information to be used in the classification calculations.



6.1.1.3. How to make classification calculations?

A. First step; following the steps described above, a table is prepared as below for the classification information obtained for all the substances forming the mixture.

Figure.6.3. First step in CLP.



Name	CAS No.	Content (%)	Classification
			CLP
Benzene	71-43-2	65	Flammable liquids,Category 2; H 225 Carcinogenicity,Category 1A; H 350 Germ cell mutagenicity,Category 1 B; H 340 Specific Target OrganToxicity(repeated exposure),Category 1; H 372 Aspiration hazard, Category 1; H 304 Eye irritation, Categort 2; H 319 Skin irritation, Category 2; H 315
Toluene	108-88-3	30	Flammable liquids,Category 2; H 225 Reproductive toxicity,Category 2; H 361d Aspiration hazard, Category 1; H 304 Specific Target OrganToxicity(repeated exposure),Category 2; H 373 Skin irritation, Category 2; H 315 Specific Target OrganToxicity(single exposure),Category 3; H 336
Xylene	1330-20-7	5	Flammable liquids,Category 3; H 226 Acute toxicity,Category 4, dermal; H 312 Acute toxicity,Category 4, inhalation; H 332 Skin irritation, Category 2; H 315

B. Second step; classification calculations;

B.1. Calculations

B.1.1. Physical hazardous calculations

B.1.1.1 Flammable liquids calculations

- In flammable liquid calculations of a mixture, flammable liquid information's of each component forming the mixture and chemical properties of the mixture should be taken into account.
- Every substance that forms a curude benzene is classified according to the explosion effect as follows;

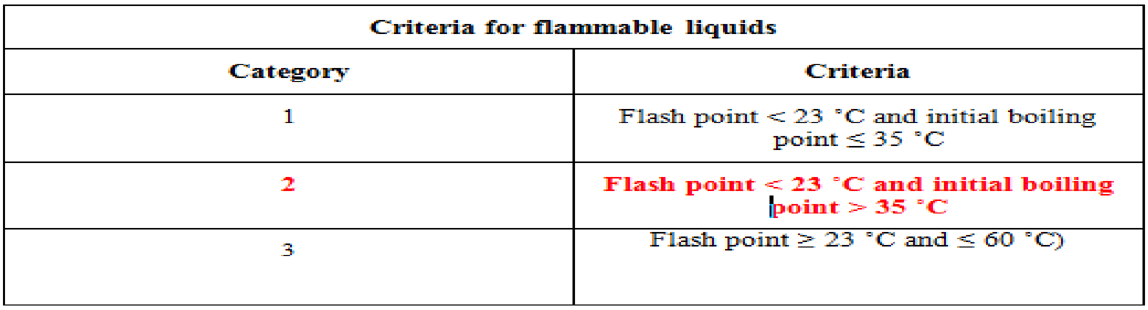
  ✓ Benzene; Flammableliquids, Category 2; H 225

- ✓ Toluene; Flammable liquids, Category 2; H 225
- ✓ Xylene; Flammable liquids, Category 2; H 225

- With it; Section 4.2.2.1 Flammable liquid for crude benzene as described; Flash point -3; For boiling point 78-80 C; Crude benzol Flammable liquid, Category 2.

Note: *Flash and boiling point informations are obtained figure.2.*

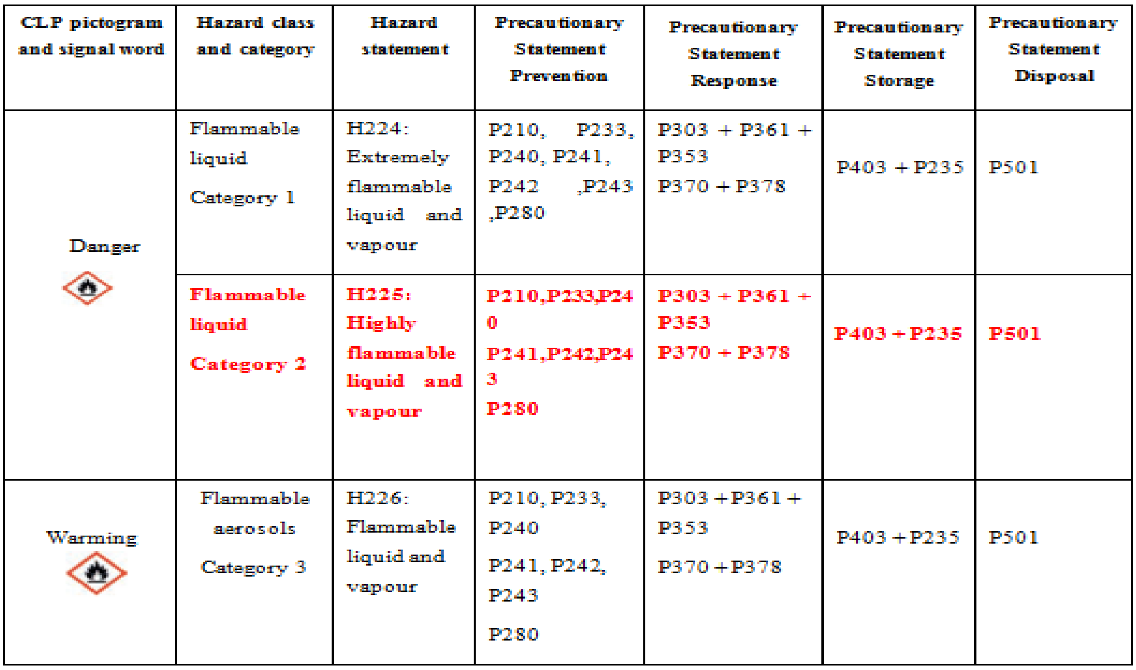
- Flammable liquid means a liquid having a flash point of not more than 60˚C.



Criteria for flammable liquids	
Category	**Criteria**
1	Flash point < 23 ˚C and initial boiling point ≤ 35 ˚C
2	**Flash point < 23 ˚C and initial boiling point > 35 ˚C**
3	Flash point ≥ 23 ˚C and ≤ 60 ˚C)

- Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for Flammable Liquids, Category 2 obtained Figure.6.4.

Figure.6.4. Physical hazards pictograms, signal words, hazard statements and precautionary statements for flammable liquids.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	Flammable liquid Category 1	H224: Extremely flammable liquid and vapour	P210, P233, P240, P241, P242 ,P243 ,P280	P303 + P361 + P353 P370 + P378	P403 + P235	P501
	Flammable liquid **Category 2**	**H225: Highly flammable liquid and vapour**	**P210,P233,P240** **P241,P242,P243** **P280**	**P303 + P361 + P353** **P370 + P378**	**P403 + P235**	**P501**
Warming	Flammable aerosols Category 3	H226: Flammable liquid and vapour	P210, P233, P240 P241, P242, P243 P280	P303 + P361 + P353 P370 + P378	P403 + P235	P501

B.1.2. Health hazardous calculations

B.1.2.1 Skin corrosion/irritation calculations

Each substance that forms crude benzol is classified according to the skin corrosion / irritation effect as follows;

- Benzene; Skin irritation, Category 2; H 315
- Toluene; Skin irritation, Category 2; H 315
- Xylene; Skin irritation, Category 2; H 315

The mixture is classified for skin corrosion/irritation if the:

Sum of (AConc / ACL) + (BConc / BCL) + …. + (ZConc / ZCL) is ≥ 1

- Where AConc = the concentration of substance A in the mixture;
- ACL = the concentration limit (either specific or generic) for substance A;
- Where BConc = the concentration of substance B in the mixture;
- clB = the concentration limit (either specific or generic) for substance B; etc.

The skin corrosion / irritation effect is calculated as:

$$= \sum (C_{Benzene} / \text{Benzene}_{CL} + C_{Toluene} / \text{Toluene}_{CL} + C_{Xylene} / \text{Xylene}_{CL})$$

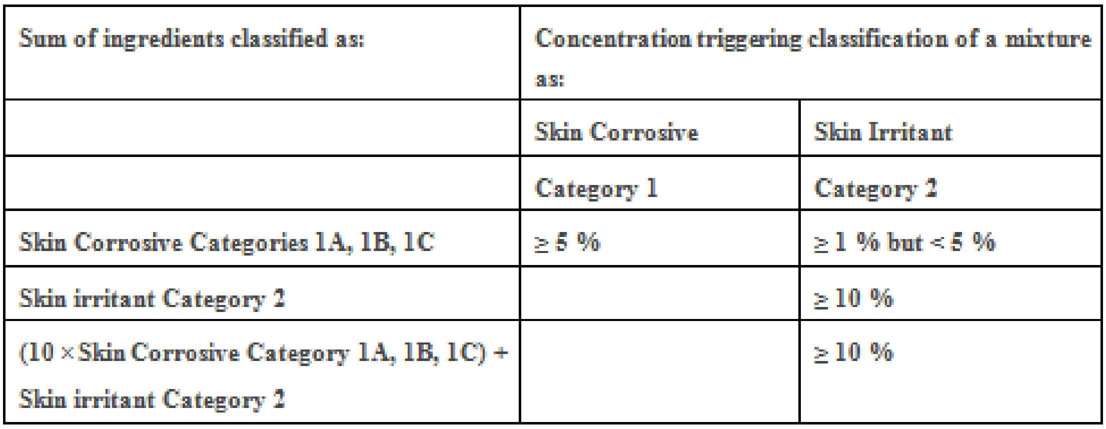
Concentration limit value from figure 5 to Category 2 is used, because all the substances forming the mixture are in category 2.

$=65/10+5/10+30/10$

$=10 \geq 1$ crude benzol takes skin irritation, category 2

Generic concentration limits of ingredients classified for skin corrosive/irritant hazard (Category 1 or 2) that trigger classification of the mixture as corrosive/irritant to skin.

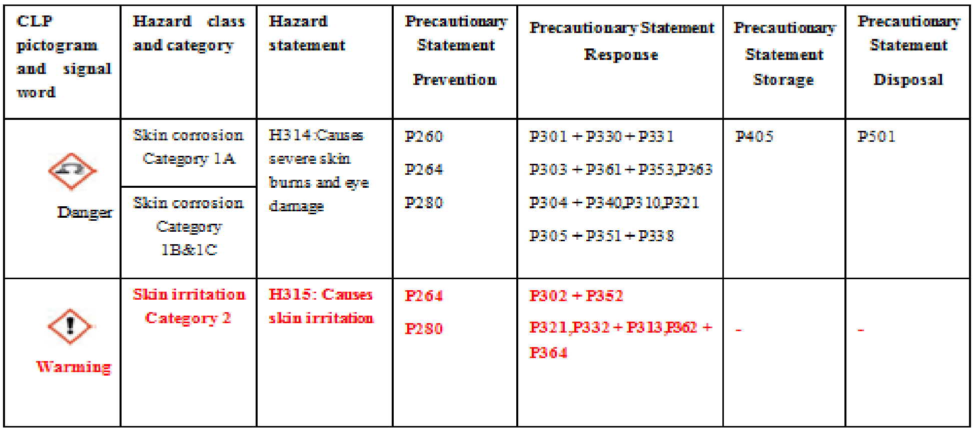
Figure. 6.5. Generic concentration limits.



Sum of ingredients classified as:	Concentration triggering classification of a mixture as:	
	Skin Corrosive	Skin Irritant
	Category 1	Category 2
Skin Corrosive Categories 1A, 1B, 1C	≥ 5 %	≥ 1 % but < 5 %
Skin irritant Category 2		≥ 10 %
(10 × Skin Corrosive Category 1A, 1B, 1C) + Skin irritant Category 2		≥ 10 %

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for skin irritation, category 2, obtained figure.6.6.

Figure.6.6. Physical hazards pictograms, signal words, hazard statements and precautionary statements for skin irritation.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	Skin corrosion Category 1A Skin corrosion Category 1B&1C	H314:Causes severe skin burns and eye damage	P260 P264 P280	P301 + P330 + P331 P303 + P361 + P353,P363 P304 + P340,P310,P321 P305 + P351 + P338	P405	P501
Warning	Skin irritation Category 2	H315: Causes skin irritation	P264 P280	P302 + P352 P321,P332 + P313,P362 + P364	-	-

B.1.2.2. Eye irritation calculations

Substances that forms a crude benzol is classified according to the eye irritation effect as follows;

Benzene; Eye irritation, Category 2; H 319

The mixture is classified for eye irritation if the:

Sum of (AConc / ACL) + (BConc / BCL) + …. + (ZConc / ZCL) is ≥1

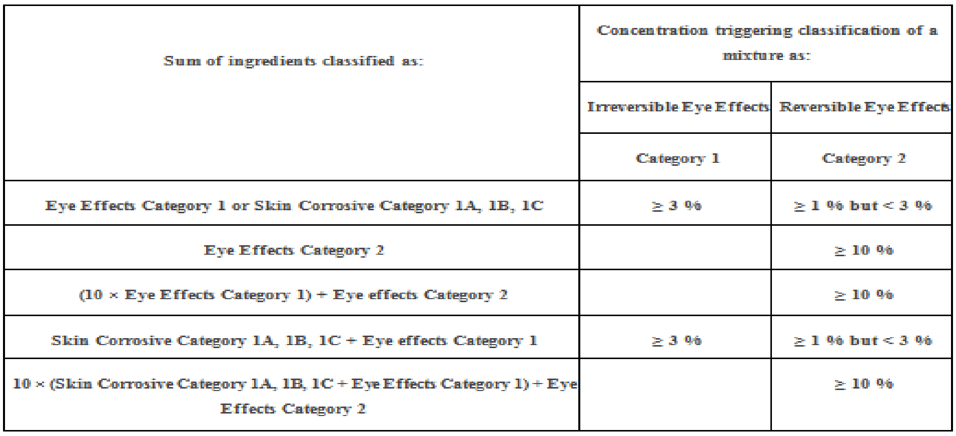
The eye irritation effect is calculated as:

$= \sum (C_{Benzene} /$ Benzene $_{CL}$

Concentration limit value from figure 7 to Category 2 is used, because all the substances forming the mixture are in category 2.

=6.5≥1 (crude benzol takes eye irritation, category 2)

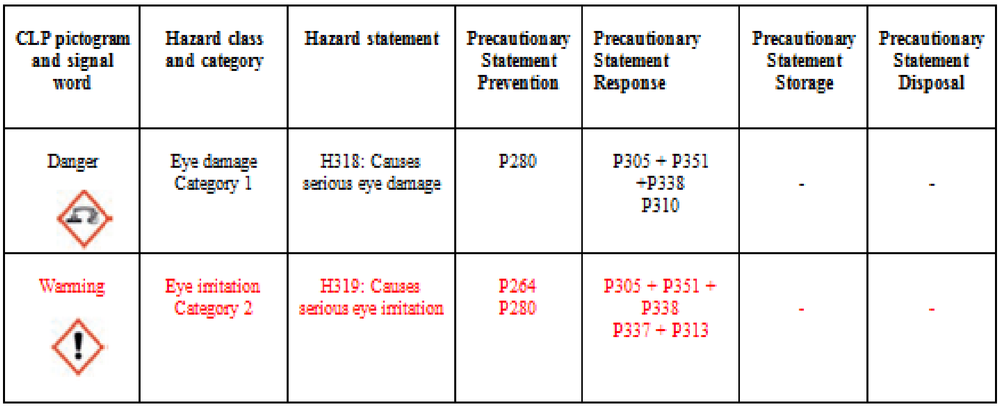
Figure.6.7. Generic concentration limits of ingredients of a mixture classified as skin corrosive category 1 and/or eye category 1 or 2 for effects on the eye that trigger classification of the mixture for effects on the eye (category 1 or 2).



Sum of ingredients classified as:	Concentration triggering classification of a mixture as:	
	Irreversible Eye Effects	Reversible Eye Effects
	Category 1	Category 2
Eye Effects Category 1 or Skin Corrosive Category 1A, 1B, 1C	≥ 3 %	≥ 1 % but < 3 %
Eye Effects Category 2		≥ 10 %
(10 × Eye Effects Category 1) + Eye effects Category 2		≥ 10 %
Skin Corrosive Category 1A, 1B, 1C + Eye effects Category 1	≥ 3 %	≥ 1 % but < 3 %
10 × (Skin Corrosive Category 1A, 1B, 1C + Eye Effects Category 1) + Eye Effects Category 2		≥ 10 %

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for eye irritation, category 2, obtained figure 6.8.

Figure.6.8. Physical hazards pictograms, signal words, hazard statements and precautionary statements for eye irritation.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	Eye damage Category 1	H318: Causes serious eye damage	P280	P305 + P351 +P338 P310	-	-
Warning	Eye irritation Category 2	H319: Causes serious eye irritation	P264 P280	P305 + P351 + P338 P337 + P313	-	-

6.1.1.4. CMR effects (Carcinoggenity) calculations

- Substances that forms a crude benzol is classified according to the CMR effects (Carcinoggenity)

effect as follows;

Benzene; Carcinogenicity, Category 1A; H 350

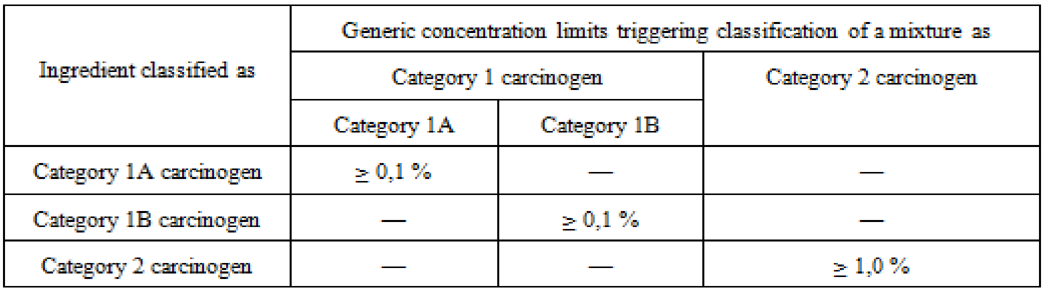
Benzene Content %65

Carcinogenicity, Category 1A; H 350

Because of the benzene concentration in the mixture is 65% and it is classified as category 1A; The mixture is classified as category 1A because the limit value ≥ 0.1 according to figure 6.9.

Generic concentration limits of ingredients of a mixture classified as carcinogen that trigger classification of the mixture.

Figure. 6.9. Generic concentration limits.



Ingredient classified as	Generic concentration limits triggering classification of a mixture as		
	Category 1 carcinogen		Category 2 carcinogen
	Category 1A	Category 1B	
Category 1A carcinogen	≥ 0,1 %	—	—
Category 1B carcinogen	—	≥ 0,1 %	—
Category 2 carcinogen	—	—	≥ 1,0 %

If a Category 2 carcinogen is present in the mixture as an ingredient at a concentration ≥ 0,1 % a SDS shall be available for the mixture upon request.

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for CMR effects (Carcinoggenity) obtained figure 6.10.

Figure. 6.10. Physical hazards pictograms.

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger 	Carciogenicity Category 1A	H350: May cause cancer	P201,P202,P280	P308 + P313	P405	P501
	Carciogenicity Category 1A					
Warning 	Carciogenicity Category 2	H351: Suspected of causing cancer	P201,P202,P280	P308 + P313	P405	P501

6.1.1.5. CMR effects (mutagenity and toxicity for reproduction) calculations

- Substances that forms a curude benzol is classified according to the CMR effects (Mutagenity and Toxicity for reproduction) as follows;

Benzene Germ cell mutagenicity, Category 1 B; H 340

- Because of the benzene concentration in the mixture is 65% and it is classified as category 1B; The mixture is classified as Category 1B since the limit value ≥ 0.1 according to Figure.6.11.

Generic concentration limits of ingredients of a mixture classified as germ cell mutagens that trigger classification of the mixture.

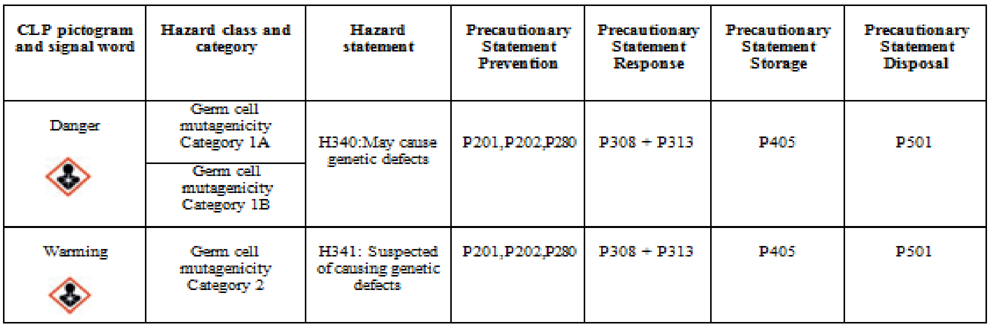
Figure.6.11. Intergradient classified.

Ingredient classified as	Concentration limits triggering classification of a mixture as		
	Category 1 mutagen		Category 2 mutagen
	Category 1A	Category 1B	
Category 1A mutagen	≥ 0,1 %	—	—
Category 1B mutagen	—	≥ 0,1 %	—
Category 2 mutagen	—	—	≥ 1,0 %

The concentration limits in the table above apply to solids and liquids (w/w units) as well as gases (v/v units).

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for CMR effects (Mutagenity and Toxicity for reproduction) obtained figure 6.12.

Figure. 12. Physical hazards pictograms.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	Germ cell mutagenicity Category 1A Germ cell mutagenicity Category 1B	H340:May cause genetic defects	P201,P202,P280	P308 + P313	P405	P501
Warning	Germ cell mutagenicity Category 2	H341: Suspected of causing genetic defects	P201,P202,P280	P308 + P313	P405	P501

6.1.1.6. STOT-single/repeated exposures calculations

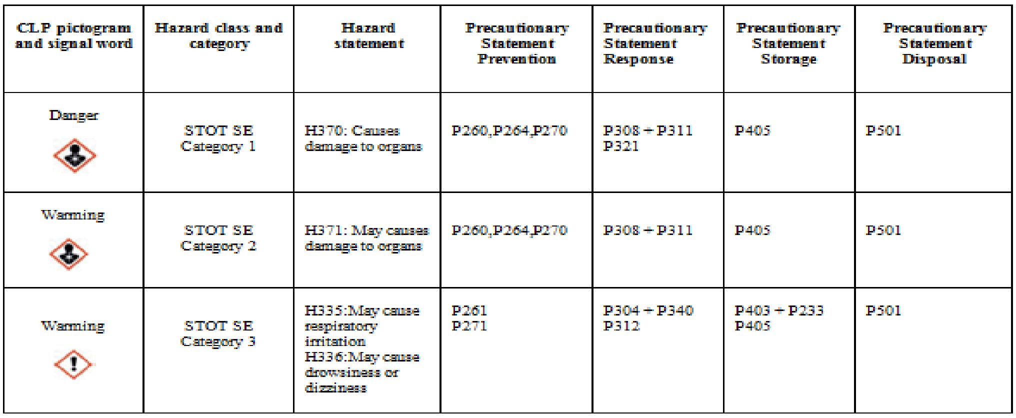
A. Single exposures

- Substances that forms a curude benzol is classified according to STOT-single effect exposures as follows;

Toluene; Specific Target OrganToxicity (single exposure), Category 3; H 336

- Because of the toluene concentration in the mixture is %30 and its concentration value is ≥ 20 C limit (CLP regulation annex I- 3.8.3.4.5); the mixture is classified as a category 3.
- According to CLP regulation annex I- 3.8.3.4.5
- Note: For category 3; the limit value is % 20
- Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for Specific target organ toxicity-single exposure, Category 3 obtained figure 6.13.

Figure.6.13. Physical hazards pictograms.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	STOT SE Category 1	H370: Causes damage to organs	P260,P264,P270	P308 + P311 P321	P405	P501
Warning	STOT SE Category 2	H371: May causes damage to organs	P260,P264,P270	P308 + P311	P405	P501
Warning	STOT SE Category 3	H335:May cause respiratory irritation H336:May cause drowsiness or dizziness	P261 P271	P304 + P340 P312	P403 + P233 P405	P501

B. STOT-repeated exposures

Substances that forms a curude benzol is classified according to STOT-repeated exposures effect as follows;

- Benzene Specific Target OrganToxicity (repeated exposure), Category 1; H 372
- Toluene Specific Target OrganToxicity (repeated exposure), Category 2; H 373

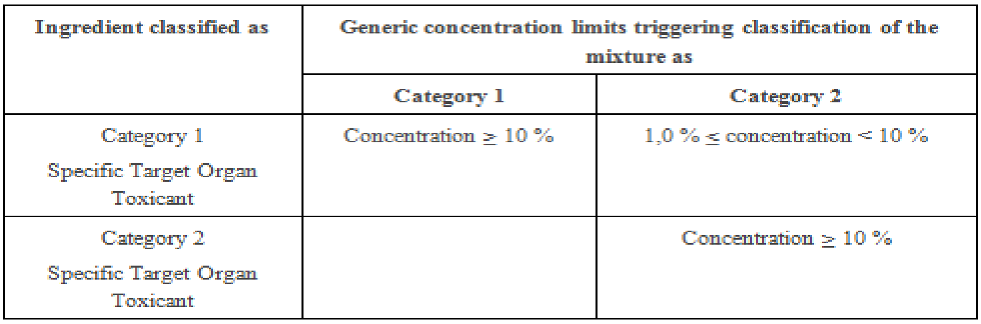
In the case of repeated exposures, the individual components of the mixture are calculated individually.

$= CBenzene/\ Benzene\ CL=65/10=6.5\geq 1$

$= C_{Toluen}/\ Toluen\ _{CL}=30/10=3\geq 1$

Because of category 1> Category 2, the crude benzene mixture is classified as category 1.

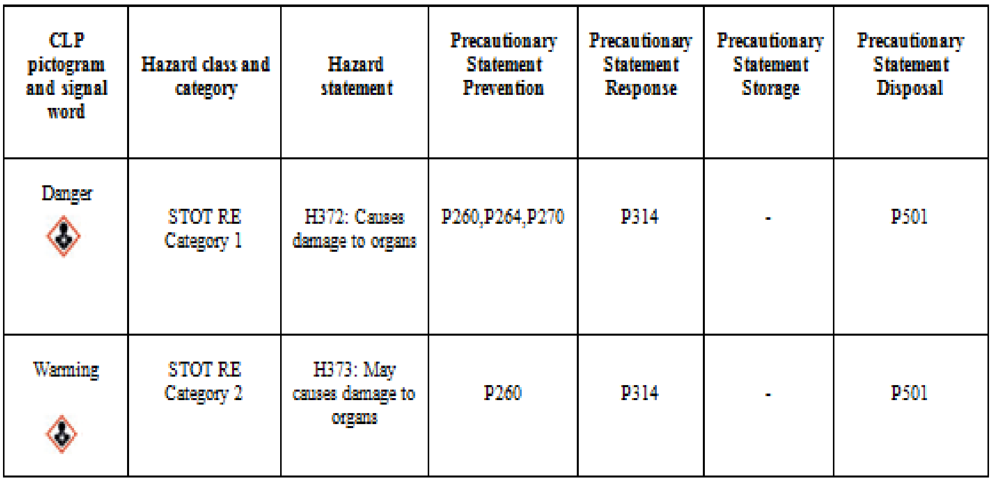
Figure. 6.14. Ingredient classified as category 1 and 2



Ingredient classified as	Generic concentration limits triggering classification of the mixture as	
	Category 1	Category 2
Category 1 Specific Target Organ Toxicant	Concentration ≥ 10 %	1,0 % ≤ concentration < 10 %
Category 2 Specific Target Organ Toxicant		Concentration ≥ 10 %

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for Specific target organ toxicity-repeated exposure, Category 1 obtained figure 6.15.

Figure. 6.15. CLP pictogram and signal word**.**



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	STOT RE Category 1	H372: Causes damage to organs	P260,P264,P270	P314	-	P501
Warning	STOT RE Category 2	H373: May causes damage to organs	P260	P314	-	P501

6.1.1.6. Aspiration calculations

- Substances that forms a curude benzol is classified according to the aspiration as follows;

Benzene Aspiration hazard, Category 1; H 304

Toluen Aspiration hazard, Category 1; H 304

Kinematic viscosity of Benzene (mm2/s) = 0,537 < 20,5 mm2 /s

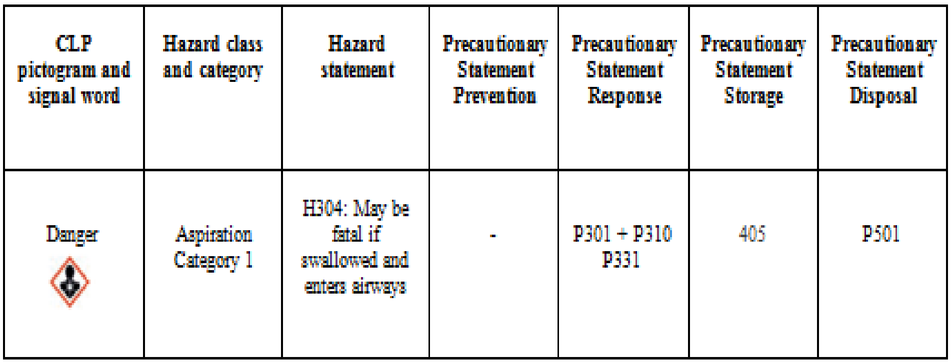
Kinematic viscosity of Toluene (mm2/s) = 0,38<20,5 mm2 /s

- A mixture which contains a total of 10 % or more of a substance or substances classified in Category 1, and has a kinematic viscosity of 20,5 mm2 /s or less, measured at 40 ˚C, shall be classified in Category 1.

So Crude Benzol is classified as a Category 1.

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for aspiration, Category1 obtained figure 6.16.

Figure. 6.16. CLP pictogram and signal word.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention	Precautionary Statement Response	Precautionary Statement Storage	Precautionary Statement Disposal
Danger	Aspiration Category 1	H304: May be fatal if swallowed and enters airways	-	P301 + P310 P331	405	P501

6.1.1.7. Acute Toxicity Calculations

- Substances that forms a crude benzol is classified according to the aspiration as follows;

Xylene, Acute toxicity, Category 4, dermal; H 312

Xylene, Acute toxicity, Category 4, inhalation; H 332

$$\frac{100}{ATE_{mix}} = \sum_{n} \frac{C_i}{ATE_i}$$

where:

Ci = concentration of ingredient i (% w/w or % v/v)

i = the individual ingredient from 1 to n

n = the number of ingredients

ATEi =Acute Toxicity Estimate of ingredient i.

Figure. 6.17. Acute toxicity hazard categories and acute toxicity estimates (ATE) defining the respective categories.

Exposure route	Category 1	Category 2	Category 3	Category 4
Oral (mg/kg bodyweight)	ATE ≤ 5	5 < ATE ≤ 50	50 < ATE ≤ 300	300 < ATE ≤ 2 000
Dermal (mg/kg bodyweight)	ATE ≤ 50	50 < ATE ≤ 200	200 < ATE ≤ 1 000	1 000 < ATE ≤ 2 000
Gases (ppmV)	ATE ≤ 100	100 < ATE ≤ 500	500 < ATE ≤ 2 500	2 500 < ATE ≤ 20 000
Vapours (mg/l)	ATE ≤ 0,5	0,5 < ATE ≤ 2,0	2,0 < ATE ≤ 10,0	10,0 < ATE ≤ 20,0
Dusts and mists (mg/l)	ATE ≤ 0,05	0,05 < ATE ≤ 0,5	0,5 < ATE ≤ 1,0	1,0 < ATE ≤ 5,0

6.1.1.9. For finding LD-Lc values

1. Use web site: http://gestis-en.itrust.de/nxt/gateway.dll/gestis_en/000000.xml?f=templates$fn=default.htm$vid=gestiseng:sdbeng$3.0

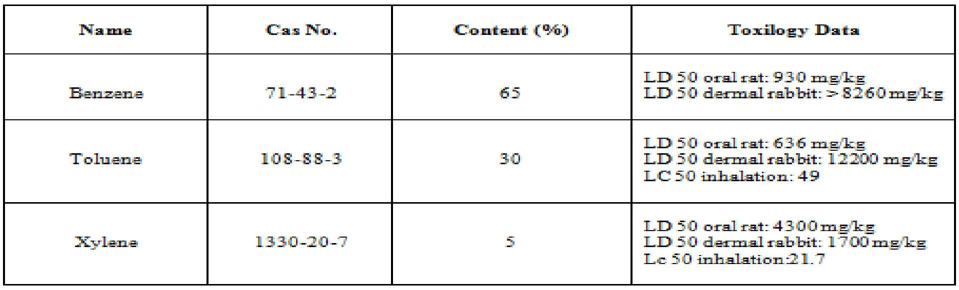
2. Open search form and write cast number and You can find toxilogy data for each component


CAS number: 1330-20-7

open search form and write cas number

For calculation write the LD50 and LC50 values of components on a table.

Figure. 6.18. Toxilogy data.



Name	Cas No.	Content (%)	Toxilogy Data
Benzene	71-43-2	65	LD 50 oral rat: 930 mg/kg LD 50 dermal rabbit: > 8260 mg/kg
Toluene	108-88-3	30	LD 50 oral rat: 636 mg/kg LD 50 dermal rabbit: 12200 mg/kg LC 50 inhalation: 49
Xylene	1330-20-7	5	LD 50 oral rat: 4300 mg/kg LD 50 dermal rabbit: 1700 mg/kg Lc 50 inhalation:21.7

A. Dermal-ATE $_{mix}$. calculations

=65/8260+30/12200+5/1700

=7,462 (Non-category)

B. Oral- ATE mix. calculations

=65/930+30/636+5/4300

=853 (Oral, Category 4)

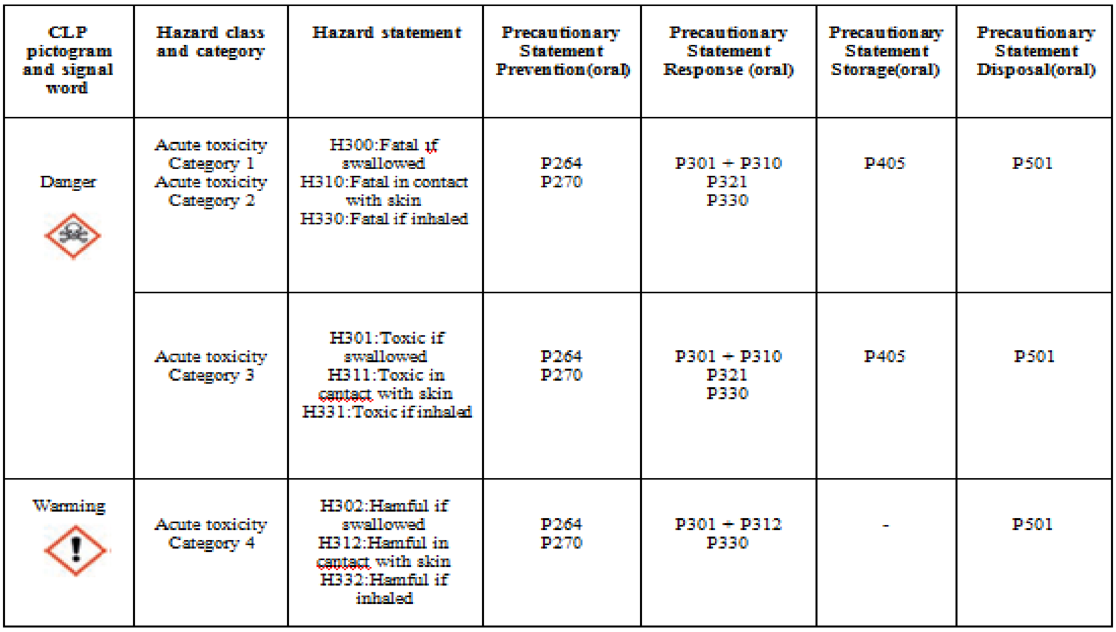
C. Inhalation calculations

=30/49+5/21.7

=118.76 (inhalation, Category 4)

- Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for acute toxicity, Oral, Category 4 obtained figure 6.19.

Figure. 6.19.CLP pictogram and signal word.



CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention(oral)	Precautionary Statement Response (oral)	Precautionary Statement Storage(oral)	Precautionary Statement Disposal(oral)
Danger	Acute toxicity Category 1 Acute toxicity Category 2	H300:Fatal if swallowed H310:Fatal in contact with skin H330:Fatal if inhaled	P264 P270	P301 + P310 P321 P330	P405	P501
	Acute toxicity Category 3	H301:Toxic if swallowed H311:Toxic in cantact with skin H331:Toxic if inhaled	P264 P270	P301 + P310 P321 P330	P405	P501
Warning	Acute toxicity Category 4	H302:Hamful if swallowed H312:Hamful in cantact with skin H332:Hamful if inhaled	P264 P270	P301 + P312 P330	-	P501

Physical Hazards Pictograms, signal words, hazard statements and precautionary statements for acute toxicity, Dermal, Category 4 obtained figure 6.20.

Figure. 6.20. CLP pictogram and signal word

CLP pictogram and signal word	Hazard class and category	Hazard statement	Precautionary Statement Prevention (dermal)	Precautionary Statement Response (dermal)	Precautionary Statement Storage(Dermal)	Precautionary Statement Disposal(dermal)
Danger 	Acute toxicity Category 1 Acute toxicity Category 2	H300:Fatal if swallowed H310:Fatal in contact with skin H330:Fatal if inhaled	P262,P264,P270 P280	P302 + P352,P310,P321 P361 + P364	P405	P501
	Acute toxicity Category 3	H301:Toxic if swallowed H311:Toxic in cantact with skin H331:Toxic if inhaled	P280	P302 + P352,P310 P321 P361 + P364	P405	P501
Warning 	Acute toxicity Category 4	H302:Hamful if swallowed H312:Hamful in cantact with skin H332:Hamful if inhaled	P280	P302 + P352 P310 P321 P361 + P364	-	P501

6.1.1.10. Results

- The Result of this case study; Classification of Crude Benzol is given figure below.

Figure. 6.21. Classification for crude benzol.

Name	Classification	
	CLP	Hazard Statement
Crude Benzol	Flammable liquids,Category 2; Carcinogenicity,Category 1A; Germ cell mutagenicity,Category 1 B; Specific Target OrganToxicity(single exposure) Category 3 Specific Target OrganToxicity(repeated exposure),Category 1 Aspiration hazard, Category 1 Eye irritation, Categort 2 Skin irritation, Category 2 Acute Toxicity Oral Category 4 Acute Toxicity İnhalation Category 4	H 225 H 350 H 340 H335 H 372 H 304 H 319 H 315 H 302,H 312,H332

6.2. Case Study (FINLAND)

6.2.1. Introduction (A real chemical accident and lessions learnt / The explosion of Lapua cartridge factory)

On dawn of April 13th 1976 took place the most devastating industrial accident in Finland. A huge explosion happened in the Finnish Defence Ministry owned Lapua ammunition factory in the town of Lapua, Finland.

40 workers were killed (most of which were women with families and children) and around 60 injured. This accident shocked the the whole nation and thousands of people took part in the funerals including the President of Finland Urho Kekkonen.

Photograph. 6.1. Rescue workers at the site of the explosion on April 13th 1976.

6.2.2. The accident

The exact time of the explosion was 7:42 AM and it occurred in the charging section of munitions. The building in which the charging section was located was completely turned in to rubble.

A major accident alert was given immediately. In an interview a local Fire Chief stated, that the explosion was heard miles away before they even got the alarm. Even at the start of the clearance works, it could be estimated, that the explosion had caused more than 40 fatal casualties. The rescue work started right away, even though there were fires still burning and causing smaller explosions.

On the day of the accident, 30 patients were transferred to the district hospital at Seinäjoki. Disaster actions were started and more staff called to work immediatly after they got the word from the explosion. Luckily the readiness to aid the victims at the hospital was good as all the surgeons of the hospital were working at the time.

A quarter of the 500 employees working in the factory were working on posts with explosion hazards. At the time of the explosion there were 69 people working in the charging section also called as ‘Lataamo II’ in which the explosion took place.

As the factory was operating for the Finnish Defence Ministry, the investigation was handed over to the Finnish Defence Forces.

Photograph. 6.2. Funeral service of the victims.

From the debris analysed, the investigators made a conclusion, that the first explosion started from a machine distributing gunpowder and spread from there as fast as 14 000 kilometres per hour in a brass tube leading to the gunpowder storage area located in the attic of the building. There was a heat activated closing device in the tube, but either it was malfunctioning or the explosion was just too fast for it to activate.

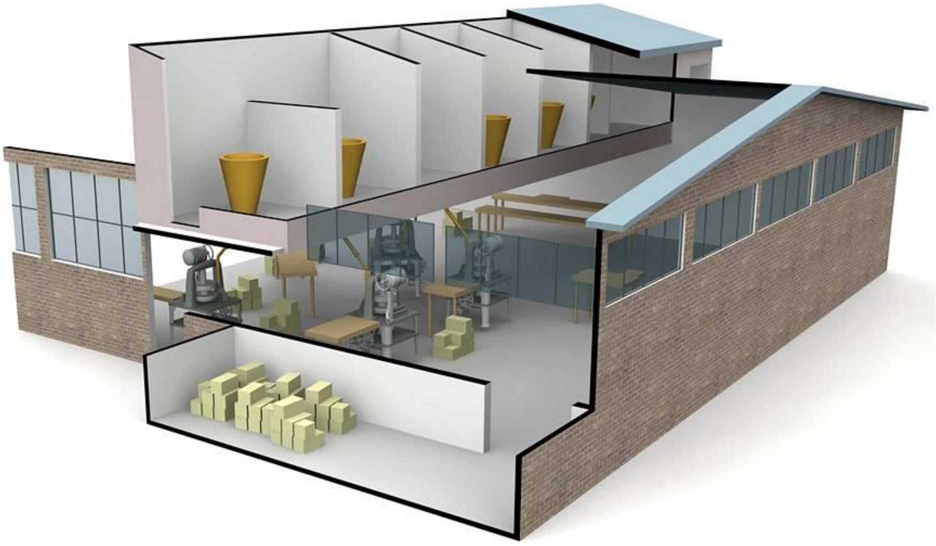
Altough it is known, where the explosion started, the reason for it is still unclear. There have been many kinds of speculations including that rust caused the machine to malfunction, foreign object in the machine had caused it or poor ventilation in the factory caused too much gunpowder to build up and was ignited by a spark.

There are two major contributing factors to the graveness of the accident.

One: the location of the gunpowder storage above the charging section. 660 to 770 kilograms of gunpowder was stored there. This was infact below the guidline amounts at the time.

Two: the distances between the buildings in the factory area were way too close according to modern safety standards.

Photograph. 6.3. The charging section and the gunpowder storage above it.



6.2.3. Consequences

Apart from the fatalities, injuries, widows and orphans, the accident caused damages to about 150 properties surrounding the factory. For compensation of damages a sum of approximately 723 000 Finnish marks was paid.

The Finnish Government gave 300 000 marks to aid the families of the victims and another 300 000 marks for the funeral arrangements.

Also a relief fund was established and it collected a hefty sum of 7,6 million marks for the families of the deceased.

In the aftermath of the disaster, new legislations with stricter safety measures in the armaments industry were introduced.

6.3. Case Study (PORTUGAL)

6.3.1. Toxic product causes explosion at SAPEC - Portugal

On dawn on Tuesday, February 16, 2017, a fire broke out at the sulphur warehouses of Sapec Agro, which was declared extinct at 9:00 am on February 16.

A total of 20 people, including 10 firefighters, suffered injuries due to the excess of sulphur dioxide released in the fire of a warehouse of this toxic product.

The excess of pollution also led to the closure, on February 16, 2017, all schools in the region.

The health authority has advised special attention to the population, such as avoiding outdoor stay or making efforts in the open air, in particular to some groups, such as children, the elderly and patients with respiratory or cardiac diseases.

More than 24 hours after the fire, sulphur dioxide was released into the atmosphere.

Photograph. 6.4. Explosion at SAPEC.

6.3.2. Explosion at BASF chemical plant in Ludwigshafen - Germany

The explosion and fire on Monday (17/10/2016) occurred a river harbour, used to unload flammable liquids and liquid gas.

Three people were killed, and 25 were severely injured.

Two people known to have died in the accident were both members of BASF's own fire brigade.

It took firefighters 10 hours to extinguish the resulting blaze. During the incident, BASF was forced to shut down 20 facilities, including two steam crackers, which produce basic hydrocarbon chemicals used to manufacture a wide range of plastics and other chemicals.

The residents located near the plant were complaining of "respiratory irritation."

A day on since the explosion, residents in Ludwigshafen and the nearby city of Mannheim were told by authorities to continue to keep all doors and windows closed. No increases of harmful substances had been reported, however.

As a safety precaution, BASF also shut down 14 other production plants on Monday and erected water barriers between the northern inland port and the Rhine.

The incident came just two years after Ludwigshafen was shaken by a devastating gas explosion, close to the BASF chemical plant. Gas transport company Gascade had been digging around a buried pipeline at the time of the blast. One excavation worker was killed and 20 other people were injured. Nearby houses and trees were burned to charcoal, leaving an entire neighbourhood devastated.

Photograph. 6.5. Explosion at BASF.

6.3.3. Explosion at Amuay refinery on 25 of August 2012

The explosion at the Amuay refinery in the Venezuelan state of Falcón caused at least 39 deaths and 86 injuries.

The explosion originated in a gas leak that affected at least two reservoirs of the refinery.

The gas build-up created a cloud that exploded and triggered fires in at least two reservoirs in the refinery and surrounding areas.

There was significant damage to infrastructure and construction around the refinery.

A total of 209 houses and 11 commercial establishments were affected in the vicinity of the refinery.

Photograph. 6.6. Explosion at Amuay Refinery.

6.3.4. Explosion causes 24 deaths at Pemex refinery in Coatzacoalcos - Mexico

The accident occurred at 3:15 pm on April 4, 2016 at the Chlorados 3 petrochemical refinery, known as Pajaritos, located in the port of Coatzacoalcos, in the eastern state of Veracruz.

After the explosion, which could be heard within a radius of 10 kilometres, the safety devices were activated, with the closure of the refinery ducts and valves, and the employees were evacuated. Civil Defence authorities withdrew 2,000 people from nearby areas and classes were suspended in six municipalities. In addition, air quality is being monitored for any substances that are hazardous to health.

Around 6:30 p.m. the fire was fully controlled, but it reiterated the call to the population not to take to the streets during the day until the gases released into the atmosphere were diluted.

Photograph. 6.7. Explosion at Pemex refinery.

6.4. Case Study (SPAIN)

6.4.1. Case identification and scope

The object of this case study is the development of the Quantitative Risk Analysis (QRA) of the Installation of a Gas Fueled Auxiliary Engine on board a Car-Ferry.

Project description

The Ferry is a Car-Ferry of 190 meters long and 26 meters breadth carrying up to 900 passengers and 247 vehicles, and operating for a 7 hours voyage.

The fuel gas installation consists of a Gas generator (GG) placed in a room located on the deck 8, a LNG tank and its Tank Connection Space (TCS) located on deck 8, and LNG and fuel gas bunker stations located on both sides on deck 3.

The GG room will be an ESD protected machinery space and will host the GG, a Bergen C26 developing a power of 1,620Mkw to 1,000rpm, the Gas Valve Unit (not in an enclosure) and the glycol water system supplying the TCS. The GG room can be accessed by means of two air locks. The glycol system is made of 2 centrifugal pumps, an electric heater for start-up and a heating loop from the engine lube-oil cooler. The vent mast is located on top of the GG room.

The LNG will be stored in a IMO-Type C vacuum insulated tank of 30m3 capacity, which supports its TCS. The LNG tank holding time before opening of the pressure safety valve (set at 10 barg) in case of no fuel gas consumption is 15 days. The TCS contains the different tank connections (liquid and vapor), a Product vaporizer and a Pressure Build-Up vaporizer. The TCS is forced ventilated

The existing bunker stations will contain connections in order to load LNG from a tank truck (LNG bunkering operation expected to take 1 hour).

Passengers are mainly boarding from the quay on deck 3, 11m aft of the bunker stations, or from the gang way on deck 5, 5m above the bunker station.

This QRA aims to determine the risk to people in the surroundings of the installation that is related to the presence of hazardous substances and for various purposes including the embarking/disembarking of passengers during bunkering operations.

The scope of the case will not be a whole QRA of the LNG plant but just to calculate the individual risk associated to 2 of the accident scenarios associated with the unloading tank module.

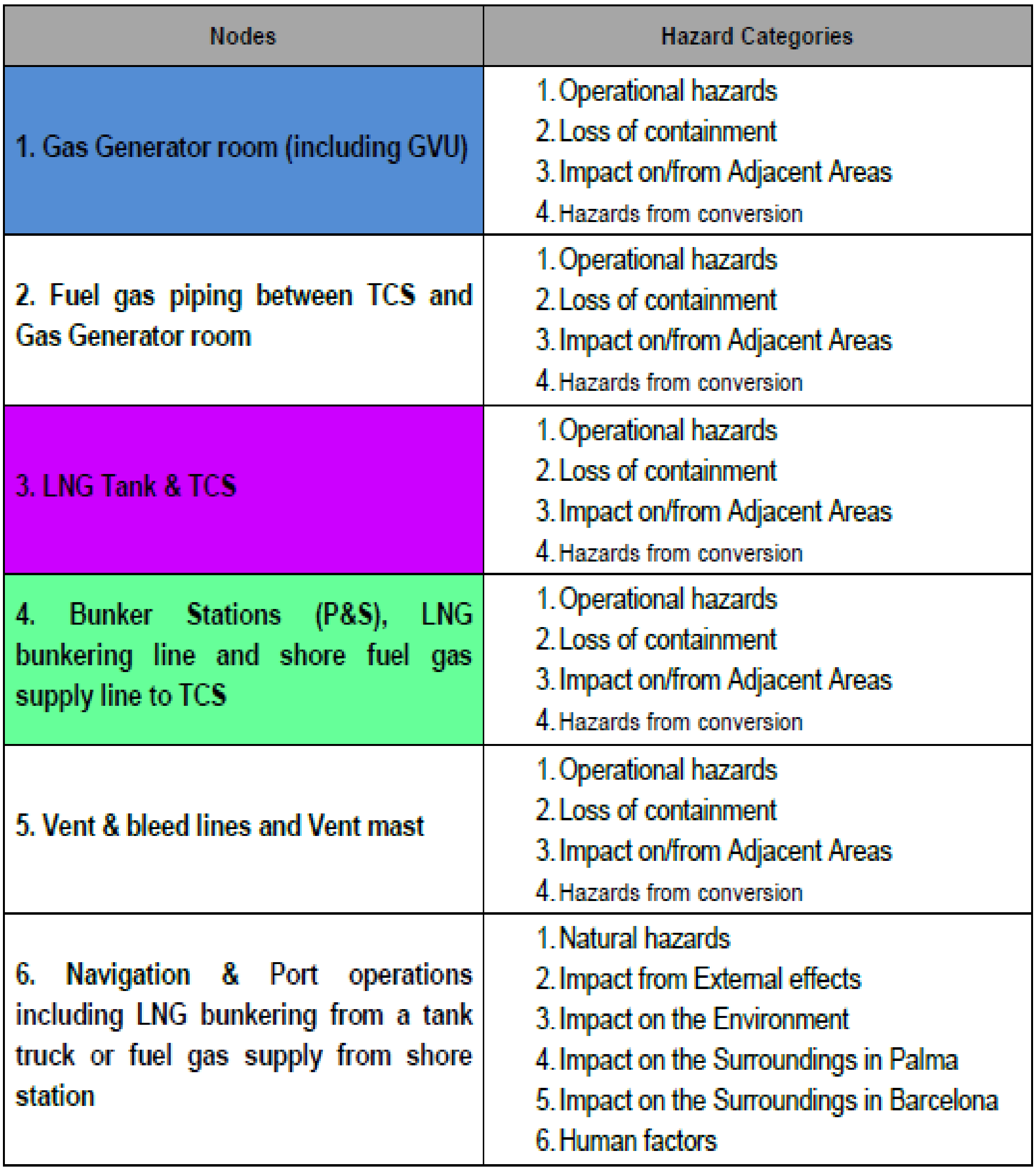
6.4.2. Risk identification

In order to follow the case, a summarize of the HAZID (methodology used for this project) results are shown below.

6.4.2.1. Nodes and hazard categories

The project is divided in to 6 nodes and their Hazard categories:

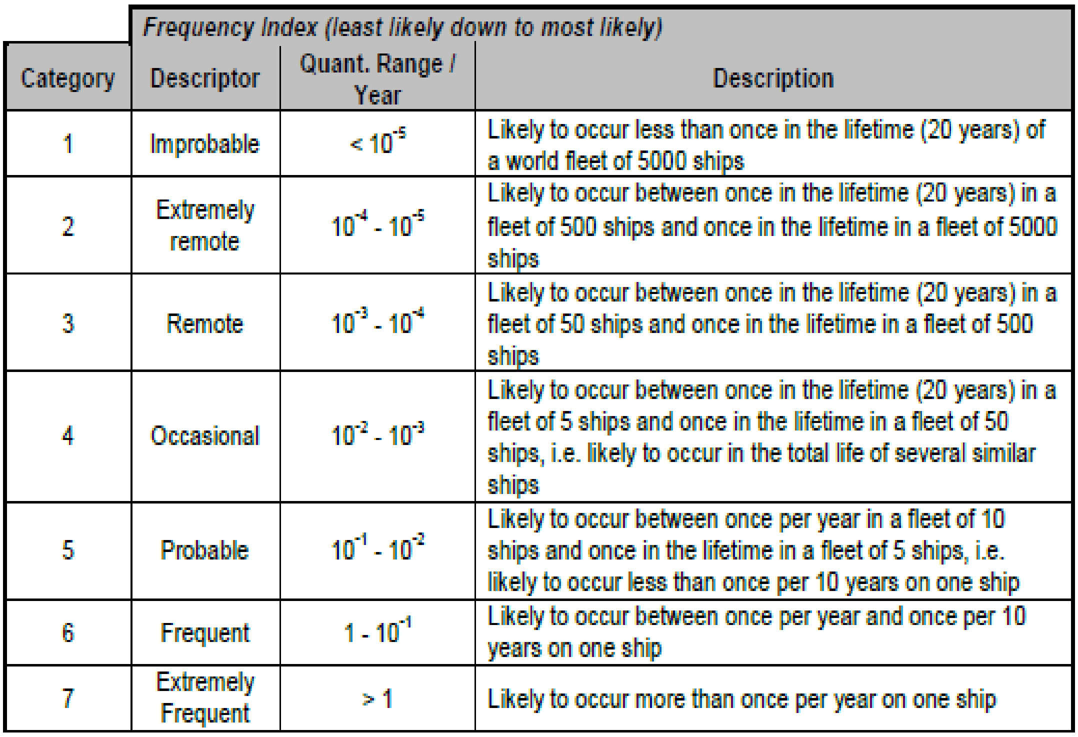
Figure.6.22. Nodes and hazard categories.



Nodes	Hazard Categories
1. Gas Generator room (including GVU)	1. Operational hazards 2. Loss of containment 3. Impact on/from Adjacent Areas 4. Hazards from conversion
2. Fuel gas piping between TCS and Gas Generator room	1. Operational hazards 2. Loss of containment 3. Impact on/from Adjacent Areas 4. Hazards from conversion
3. LNG Tank & TCS	1. Operational hazards 2. Loss of containment 3. Impact on/from Adjacent Areas 4. Hazards from conversion
4. Bunker Stations (P&S), LNG bunkering line and shore fuel gas supply line to TCS	1. Operational hazards 2. Loss of containment 3. Impact on/from Adjacent Areas 4. Hazards from conversion
5. Vent & bleed lines and Vent mast	1. Operational hazards 2. Loss of containment 3. Impact on/from Adjacent Areas 4. Hazards from conversion
6. Navigation & Port operations including LNG bunkering from a tank truck or fuel gas supply from shore station	1. Natural hazards 2. Impact from External effects 3. Impact on the Environment 4. Impact on the Surroundings in Palma 5. Impact on the Surroundings in Barcelona 6. Human factors

6.4.2.2. Likelihood

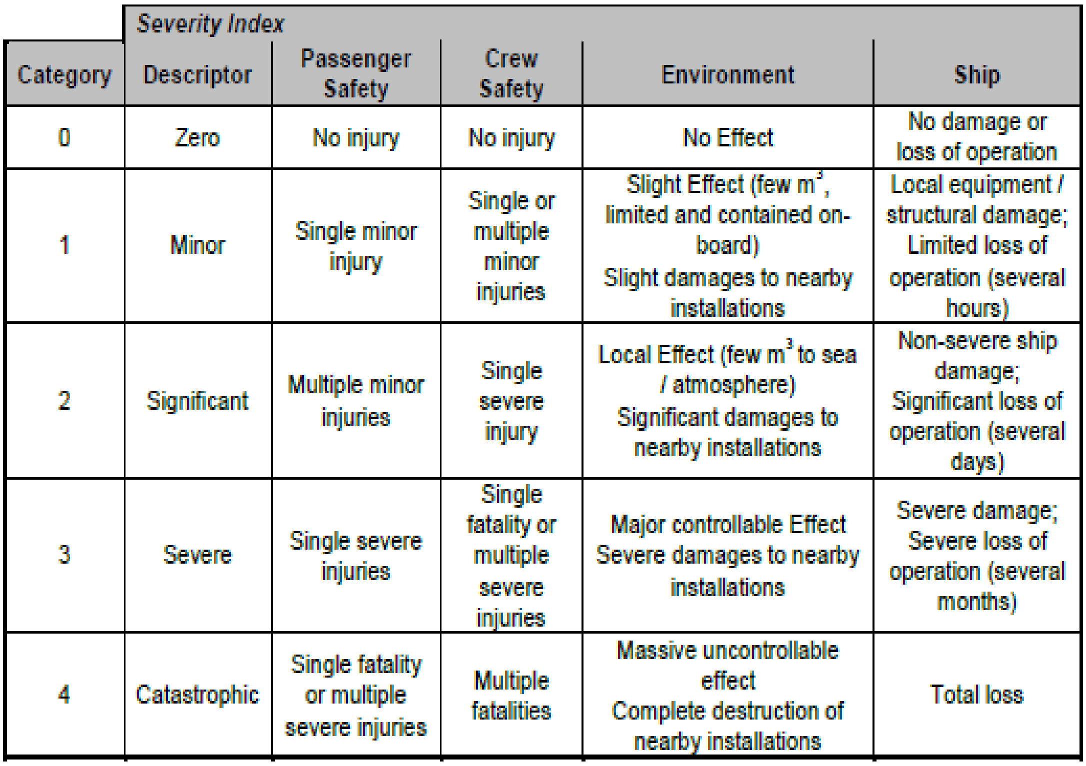
Figure.6.23. Likelihood.



	Frequency Index (least likely down to most likely)		
Category	Descriptor	Quant. Range / Year	Description
1	Improbable	$< 10^{-5}$	Likely to occur less than once in the lifetime (20 years) of a world fleet of 5000 ships
2	Extremely remote	$10^{-4} - 10^{-5}$	Likely to occur between once in the lifetime (20 years) in a fleet of 500 ships and once in the lifetime in a fleet of 5000 ships
3	Remote	$10^{-3} - 10^{-4}$	Likely to occur between once in the lifetime (20 years) in a fleet of 50 ships and once in the lifetime in a fleet of 500 ships
4	Occasional	$10^{-2} - 10^{-3}$	Likely to occur between once in the lifetime (20 years) in a fleet of 5 ships and once in the lifetime in a fleet of 50 ships, i.e. likely to occur in the total life of several similar ships
5	Probable	$10^{-1} - 10^{-2}$	Likely to occur between once per year in a fleet of 10 ships and once in the lifetime in a fleet of 5 ships, i.e. likely to occur less than once per 10 years on one ship
6	Frequent	$1 - 10^{-1}$	Likely to occur between once per year and once per 10 years on one ship
7	Extremely Frequent	> 1	Likely to occur more than once per year on one ship

6.4.2.3. Consequence severity

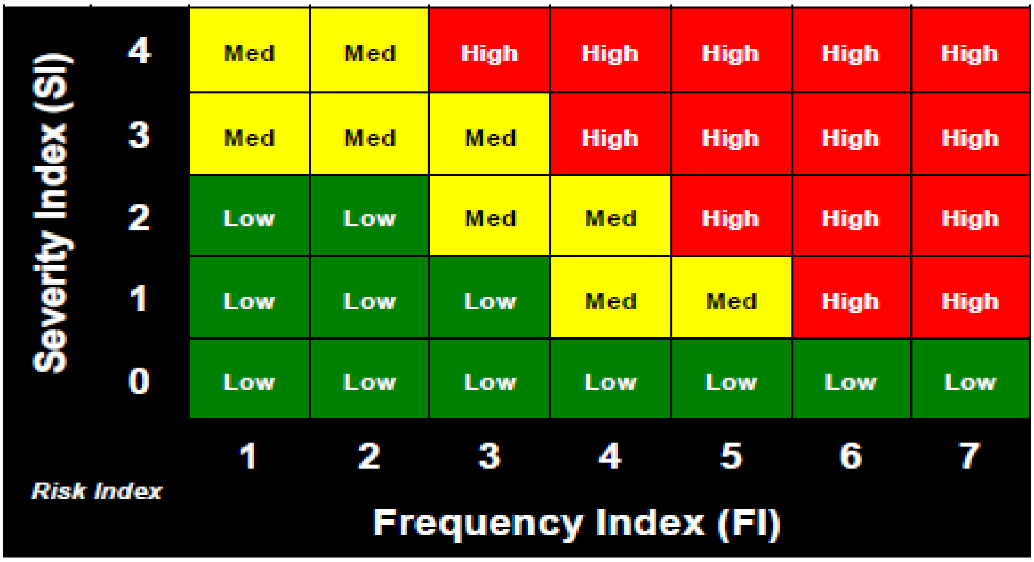
Figure.6.24. Consequence severity.



	Severity Index				
Category	Descriptor	Passenger Safety	Crew Safety	Environment	Ship
0	Zero	No injury	No injury	No Effect	No damage or loss of operation
1	Minor	Single minor injury	Single or multiple minor injuries	Slight Effect (few m^3, limited and contained on-board) Slight damages to nearby installations	Local equipment / structural damage; Limited loss of operation (several hours)
2	Significant	Multiple minor injuries	Single severe injury	Local Effect (few m^3 to sea / atmosphere) Significant damages to nearby installations	Non-severe ship damage; Significant loss of operation (several days)
3	Severe	Single severe injuries	Single fatality or multiple severe injuries	Major controllable Effect Severe damages to nearby installations	Severe damage; Severe loss of operation (several months)
4	Catastrophic	Single fatality or multiple severe injuries	Multiple fatalities	Massive uncontrollable effect Complete destruction of nearby installations	Total loss

6.4.2.4. Risk ranking matrix

Figure.6.25. Risk ranking matrix.



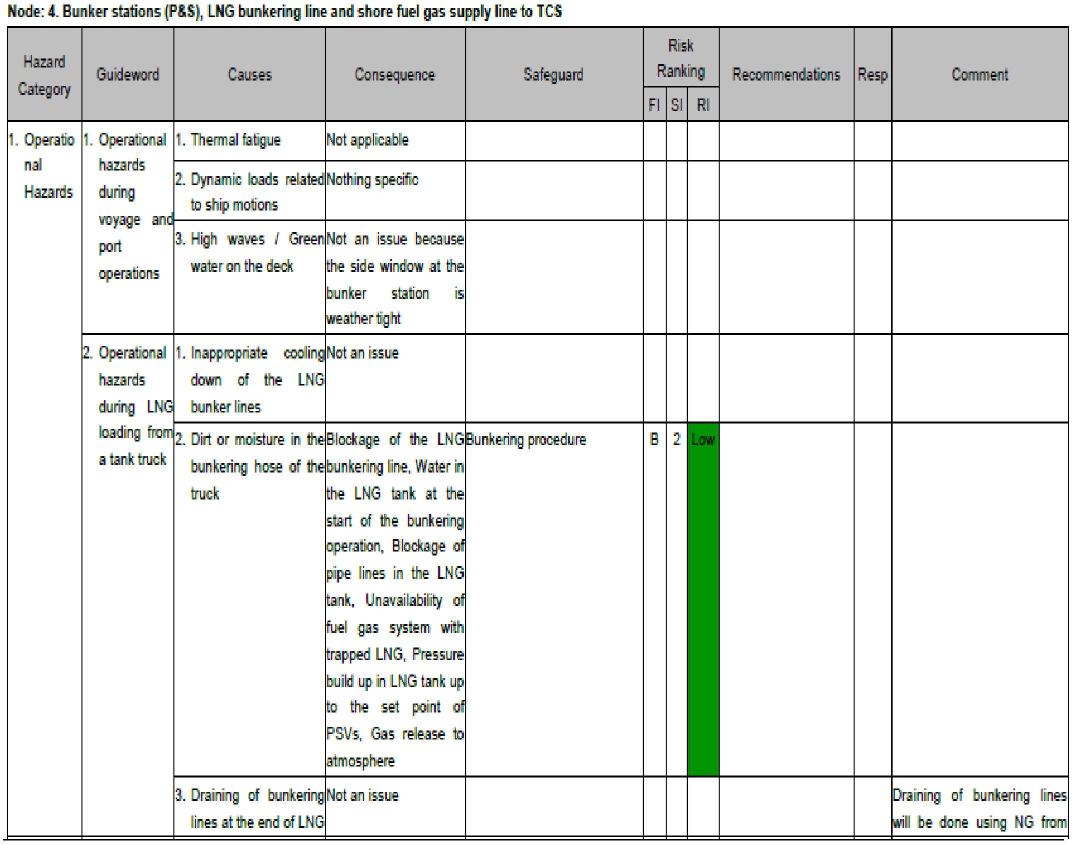
Severity Index (SI)							
4	Med	Med	High	High	High	High	High
3	Med	Med	Med	High	High	High	High
2	Low	Low	Med	Med	High	High	High
1	Low	Low	Low	Med	Med	High	High
0	Low	Low	Low	Low	Low	Low	Low
Risk Index	1	2	3	4	5	6	7

Frequency Index (FI)

6.4.2.5. Example of HAZID report

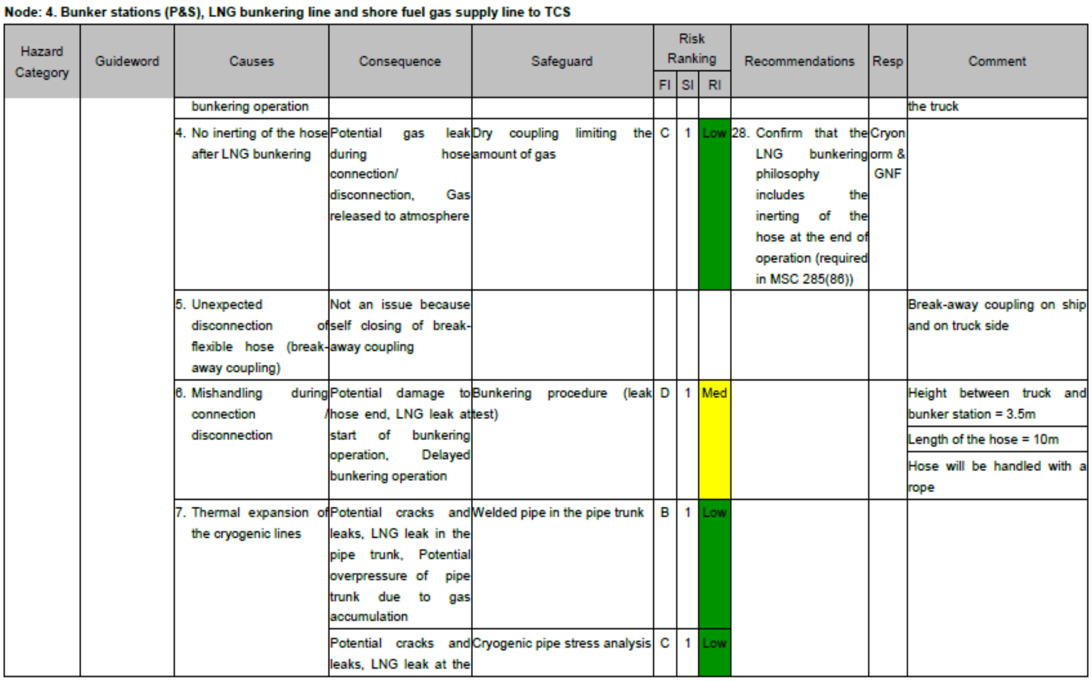
An example of the HAZID report (2 consecutive pages) for node 4 is shown below to follow the HAZID methodology used in the project.

Figure.6.26. HAZID example sheets.



Node: 4. Bunker stations (P&S), LNG bunkering line and shore fuel gas supply line to TCS

Hazard Category	Guideword	Causes	Consequence	Safeguard	Risk Ranking			Recommendations	Resp	Comment
					FI	SI	RI			
1. Operational Hazards	1. Operational hazards during voyage and port operations	1. Thermal fatigue	Not applicable							
		2. Dynamic loads related to ship motions	Nothing specific							
		3. High waves / Green water on the deck	Not an issue because the side window at the bunker station is weather tight							
	2. Operational hazards during LNG loading from a tank truck	1. Inappropriate cooling down of the LNG bunker lines	Not an issue							
		2. Dirt or moisture in the bunkering hose of the truck	Blockage of the LNG bunkering line, Water in the LNG tank at the start of the bunkering operation, Blockage of pipe lines in the LNG tank, Unavailability of fuel gas system with trapped LNG, Pressure build up in LNG tank up to the set point of PSVs, Gas release to atmosphere	Bunkering procedure	B	2	Low			
		3. Draining of bunkering lines at the end of LNG	Not an issue							Draining of bunkering lines will be done using NG from



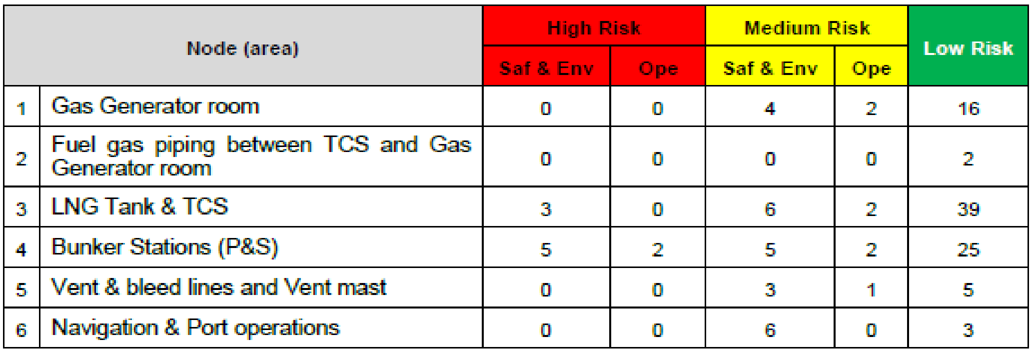
Node: 4. Bunker stations (P&S), LNG bunkering line and shore fuel gas supply line to TCS

Hazard Category	Guideword	Causes	Consequence	Safeguard	Risk Ranking			Recommendations	Resp	Comment
					FI	SI	RI			
		bunkering operation								the truck
		4. No inerting of the hose after LNG bunkering	Potential gas leak during hose connection/ disconnection, Gas released to atmosphere	Dry coupling limiting the amount of gas	C	1	Low 🟩	28. Confirm that the LNG bunkering philosophy includes the inerting of the hose at the end of operation (required in MSC 285(86))	Cryonorm & GNF	
		5. Unexpected disconnection of flexible hose (break-away coupling)	Not an issue because self closing of break-away coupling							Break-away coupling on ship and on truck side
		6. Mishandling during connection / disconnection	Potential damage to hose end, LNG leak at start of bunkering operation, Delayed bunkering operation	Bunkering procedure (leak test)	D	1	Med 🟨			Height between truck and bunker station = 3.5m Length of the hose = 10m Hose will be handled with a rope
		7. Thermal expansion of the cryogenic lines	Potential cracks and leaks, LNG leak in the pipe trunk, Potential overpressure of pipe trunk due to gas accumulation	Welded pipe in the pipe trunk	B	1	Low 🟩			
			Potential cracks and leaks, LNG leak at the	Cryogenic pipe stress analysis	C	1	Low 🟩			

6.4.2.6. Conclusions

Out of 131 studied scenarios, there are 10 scenarios falling in the "High risk" area (after application of existing safeguards).

Figure.6.27. Conclusions of HAZID.



	Node (area)	High Risk 🟥		Medium Risk 🟨		Low Risk 🟩
		Saf & Env	Ope	Saf & Env	Ope	
1	Gas Generator room	0	0	4	2	16
2	Fuel gas piping between TCS and Gas Generator room	0	0	0	0	2
3	LNG Tank & TCS	3	0	6	2	39
4	Bunker Stations (P&S)	5	2	5	2	25
5	Vent & bleed lines and Vent mast	0	0	3	1	5
6	Navigation & Port operations	0	0	6	0	3

The 10 high risks are concentrated in Node 3 LNG Tank & TCS and Node 4 Bunkering Stations (P&S) due to 4 main raisons:

- The presence of passengers and cars on deck 8 during embarkment/loading/parking near-by the hazardous area created by the LNG tanks and the TCS.
- The simultaneous operation of bunkering LNG and having passengers embarking from the aft door on deck 3 or the gangway on deck 5.

- Other operations carried out at the bunker stations (MDO or fresh water bunkering) concurrently with LNG bunkering or shore fuel gas supply operation.
- Massive gas release in non-hazardous area such as on deck 7 from pipe trunk of fuel gas line from shore.

6.4.3. Risk estimation

6.4.3.1. Scenario list

After complete understanding of the equipment of the installation in the previous preliminary analysis (Risk Identification), documentation and the experience in this sector, and subject to such definition given in the BEVI for the purpose of selection of initiators scenarios, a selection can be made of postulated events initiators, which collect those events with a reasonable probability of occurrence and, a priori, more severe consequences in the surroundings of the facility.

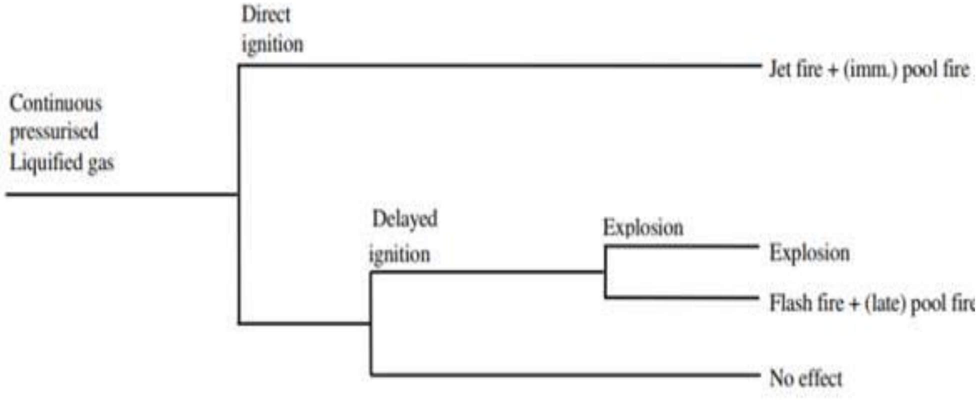
In total, 2 initiating events have been identified for analysis in this case, which according to its evolution will result in various accident scenarios (jet fire, vapor cloud explosion unconfined, flares, etc.).

Table.6.1. Scenario list.

ID CODE	Substance	Initiating events
HOS. 1	LNG	**Rupture of unloading LNG cryogenic hose.**
HOS. 2	LNG	**Leak in unloading LNG cryogenic hose with an effective diameter of 10% of the nominal diameter, up to a maximum of 50mm.**

6.4.3.2. Identification of dangerous phenomena associated

Figure.6.28. Dangerous phenomena tree.



6.4.3.3. Determination of causes and frequency of initiating events

The following summarizes the main causes that can take place for each initiating event. Initiating events of a similar type are grouped to reflect causes.

The causes were obtained by consulting bibliographic reference sources, the identification of initiating events previously made and the HAZID results.

Table.6.2. Causes of the initial events.

Initiating event	ID Code	Causes
Rupture of unloading LNG hose.	HOS.1 HOS.2	- Failure of hose connections. - Failure of operations (bad connection, opening wrong valves, etc.) - Collision with vehicles or movement while being unloaded, with broken connections or tanks on trucks. - Sabotage - Human errors.

The initiating events frequencies are determined by application of direct standard values given in sections 3.4 to 3.15 of BEVI manual.

For those initiating events whose probability depends on the number of operations performed, length of piping, etc., the frequency of the final event on the occasion / year was calculated depending on the time the operation is performed, the length of the pipe, the total number of similar existing equipment at the facility, etc.

Table.6.3. Frequency of the initial events.

Initiating event	Basic frequency	Marks	Final Frequency (oc./year)
HOS. 1 Rupture of unloading LNG hose.	$4 \cdot 10^{-6}$/hour	Presence of the tank truck at the installation approximately 78 hours per year (52 tank trucks per year)	$78\times 4\cdot10^{-6} = 3{,}12\cdot10^{-4}$
HOS. 2 Leak in unloading LNG hose with an effective diameter of 10% of the nominal diameter.	$4 \cdot 10^{-5}$/hour	Presence of the tank truck at the installation approximately 78 hours per year (52 tank trucks per year)	$78\times 4\cdot10^{-5} = 3{,}12\cdot10^{-3}$

6.4.3.4. Frequency modifiers

The unloading operation is supervised by 2 operators of the ferry (1 onshore with the truck driver and 1 in the ferry) and the truck driver. In case of accident or malfunction either the truck driver can push the emergency buttons in the truck (3 emergency buttons: 1 in each side of the truck and 1 at the back) stopping the pump and the unloading, or the operator can push the ESD associated to the unloading in the TCS.

Respect the determination of ignition probabilities (direct and delayed probabilities):

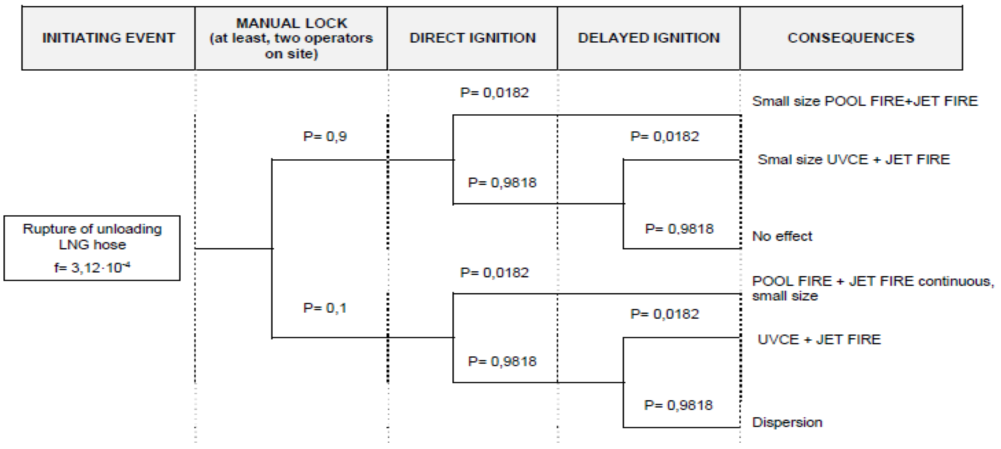
- The values have been identified from International Association of Oil and Gas Producers (OGP-434-01 March 2010). Based on the available OGP models, the “UKOOA – Scenario 24 FPSO Gas” model was considered to be best suited for this analysis, especially since release LNG would propagate on an open deck, similarly to a comparable leak on a large LNG ship.
- The “UKOOA – Scenario 5 Small Plant Gas LPG” (OGP-434-01 March 2010) model was considered for HOS 1 and HOS 2 scenarios.

6.4.3.5. Event tree analysis

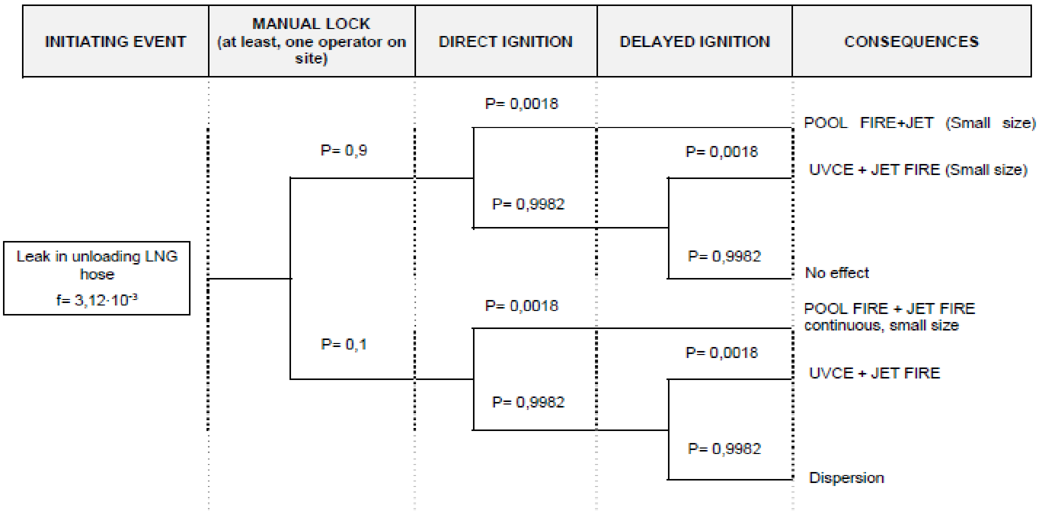
Then the event trees associated to the scenarios chosen are:

Figure.6.29. Case study: Event trees.

HOS. 1 Rupture of unloading LNG hose



HOS. 2 Leak in unloading LNG hose with an effective diameter of 10% of the nominal diameter



6.4.3.6. Table of final frequencies accidents

The following table summarizes which it is collected for each initiating event of final accidents frequencies shown. In those trees whose events in different ways they can achieve consequences of the same type, only frequencies most critical of these situations are listed in the following table.

Table.6.4. Final frequencies of accidents.

Initiating event	Initial frequency (oc./yr)	Event tree No.	Final accidents	Probability	Final frequency of accident
HOS. 1: Rupture of unloading LNG hose.	$3{,}12 \cdot 10^{-4}$	Tree 1	UVCE + Jet Fire	0,0164	$5{,}11 \cdot 10^{-6}$
HOS. 2: Leak in unloading LNG hose with an effective diameter of 10% of the nominal diameter, up to a maximum of 50mm.	$3{,}12 \cdot 10^{-3}$	Tree 2	UVCE + Jet Fire	0,0016	$5{,}05 \cdot 10^{-6}$

6.4.3.7. Consequences models

QRA Consequences Calculation for each of the initiating events analyzed previously are shown in Annex I, following the methodology identify in the course.

6.4.3.8. Vulnerability modelling

The analysis of vulnerability due to hazardous phenomena associated with major accidents is done by applying the "Probit methodology", following the methodology identify in the course:

6.4.3.9. Individual risk

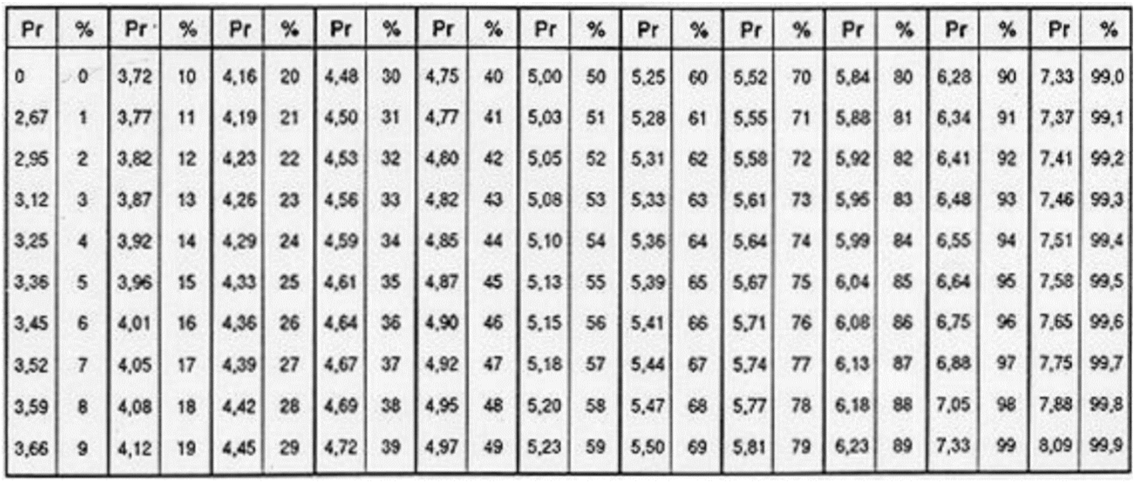
In order to draw risk curves has followed the methodology described below:

- The damage associated to each curve represents risk to be calculated.

Damage = Risk (curve value) / Frequency of accident

- Then, the value in the table of equivalence between values "Probit" and percentage of population affected (damage) is introduced, obtaining the value "Probit" in question for each curve.

Figure.6.30. Equivalence between values "Probit" and percentage of population affected.



Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%	Pr	%
0	0	3,72	10	4,16	20	4,48	30	4,75	40	5,00	50	5,25	60	5,52	70	5,84	80	6,28	90	7,33	99,0
2,67	1	3,77	11	4,19	21	4,50	31	4,77	41	5,03	51	5,28	61	5,55	71	5,88	81	6,34	91	7,37	99,1
2,95	2	3,82	12	4,23	22	4,53	32	4,80	42	5,05	52	5,31	62	5,58	72	5,92	82	6,41	92	7,41	99,2
3,12	3	3,87	13	4,26	23	4,56	33	4,82	43	5,08	53	5,33	63	5,61	73	5,95	83	6,48	93	7,46	99,3
3,25	4	3,92	14	4,29	24	4,59	34	4,85	44	5,10	54	5,36	64	5,64	74	5,99	84	6,55	94	7,51	99,4
3,36	5	3,96	15	4,33	25	4,61	35	4,87	45	5,13	55	5,39	65	5,67	75	6,04	85	6,64	95	7,58	99,5
3,45	6	4,01	16	4,36	26	4,64	36	4,90	46	5,15	56	5,41	66	5,71	76	6,08	86	6,75	96	7,65	99,6
3,52	7	4,05	17	4,39	27	4,67	37	4,92	47	5,18	57	5,44	67	5,74	77	6,13	87	6,88	97	7,75	99,7
3,59	8	4,08	18	4,42	28	4,69	38	4,95	48	5,20	58	5,47	68	5,77	78	6,18	88	7,05	98	7,88	99,8
3,66	9	4,12	19	4,45	29	4,72	39	4,97	49	5,23	59	5,50	69	5,81	79	6,23	89	7,33	99	8,09	99,9

- Then, the Probit value (for mortality of 1%, 50% and 99%), is cleared of the equation that is applicable in these cases should be chosen depending on the type of accident, the following equations:
- Heat Radiation – fatal burns (without protective clothes)

$$- \qquad Pr = -14{,}9 + 2{,}56 \cdot \ln (I^{4{,}3} \cdot t * 10^{-4})$$

Where:

- ✓ Pr: Probit equation value
- ✓ I: Heat radiation W/m^2
- ✓ t: exposure time in sec.

- Overpressure – death from pulmonary hemorrhage (wave peak)

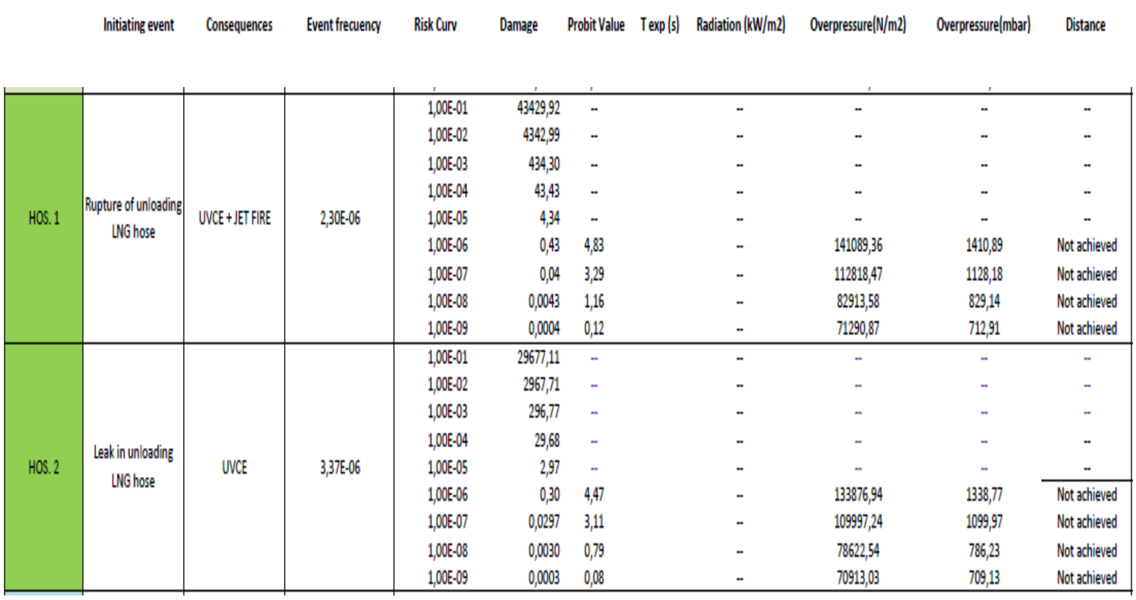
Where:

- ✓ Pr: Probit equation value
- ✓ P: Maximum overpressure N/m^2

- Once R (thermal radiation) and P (pressure) value is known, it obtained the curves of these values vs distance drawing in the calculation of consequences (Annex I) for each scenario through software EFFECTS, obtaining on the distance from which the value of the frequency of death.
- Then, once all values obtained all the proposed scenarios are achieved isoriesgo draw curves of the installation.

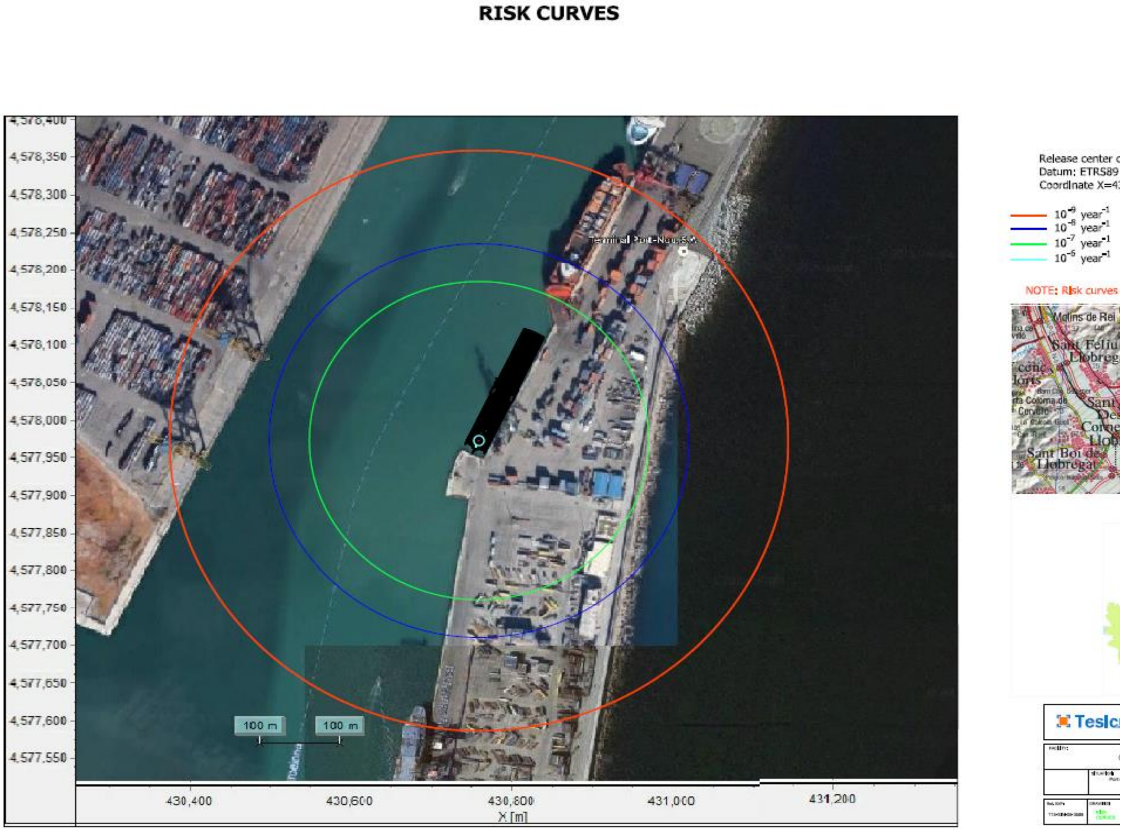
The table below is calculated with the data obtained following this methodology for each scenario. In the figure are shown the risk curves for the installation (frequency curves of 10^{-6}, 10^{-7}, 10^{-8} y 10^{-9}).

Figure.6.31. Damage calculation.



	Initiating event	Consequences	Event frecuency	Risk Curv	Damage	Probit Value	T exp (s)	Radiation (kW/m2)	Overpressure(N/m2)	Overpressure(mbar)	Distance
HOS. 1	Rupture of unloading LNG hose	UVCE + JET FIRE	2,30E-06	1,00E-01	43429,92	--		--	--	--	--
				1,00E-02	4342,99	--		--	--	--	--
				1,00E-03	434,30	--		--	--	--	--
				1,00E-04	43,43	--		--	--	--	--
				1,00E-05	4,34	--		--	--	--	--
				1,00E-06	0,43	4,83		--	141089,36	1410,89	Not achieved
				1,00E-07	0,04	3,29		--	112818,47	1128,18	Not achieved
				1,00E-08	0,0043	1,16		--	82913,58	829,14	Not achieved
				1,00E-09	0,0004	0,12		--	71290,87	712,91	Not achieved
HOS. 2	Leak in unloading LNG hose	UVCE	3,37E-06	1,00E-01	29677,11	--		--	--	--	--
				1,00E-02	2967,71	--		--	--	--	--
				1,00E-03	296,77	--		--	--	--	--
				1,00E-04	29,68	--		--	--	--	--
				1,00E-05	2,97	--		--	--	--	--
				1,00E-06	0,30	4,47		--	133876,94	1338,77	Not achieved
				1,00E-07	0,0297	3,11		--	109997,24	1099,97	Not achieved
				1,00E-08	0,0030	0,79		--	78622,54	786,23	Not achieved
				1,00E-09	0,0003	0,08		--	70913,03	709,13	Not achieved

Figure.6.32. Isocurves drawing.



6.4.4. Risk evaluation

In this section, individual risk curve obtained for the installation is compared with criteria of acceptability of individual risk.

From Formal Safety Assessment FSA – RoPax Ships MSC85/17/2 of International Maritime Organization IMO, the following outlines the acceptance criteria used in this study for individual risk for passenger members. Individual risk is usually expressed as the frequency of an individual fatality per year. These criteria is the following for passengers.

Maximum tolerable risk for passengers (risk below this limit should be made ALARP) is 10^{-4} per year.

6.4.5. Conclusıons

The bunkering and unloading operations do not reach values to defined risk curves in these scenarios. Only individual risk curves were obtained 10^{-6}, 10^{-7},10^{-8} y 10^{-9} year $^{-1}$ for TCS and LNG module, so the risk at the facility for passengers is lower than the acceptability criteria described in Formal Safety Assessment FSA of International Maritime Organization IMO.

In summary, there is no individual risk to passengers during bunkering operations in bunker station and unloading areas. Only in TCS module exists individual risk to passengers, but the risk is lower than the acceptability criteria described in Formal Safety Assessment of IMO.

6.4.6. Case study: Consequences modeling for Installation of a Gas Fueled Auxiliary Engine

6.4.6.1. Behavior of substance

Accidents associated with LNG, are shown in 6.4.3.2.

6.4.6.2. Methodology of consequences models

Defined in the course.

6.4.6.3. Assumptions related to study events

- Holes breakpoints

The holes breakpoints will be simulated with circular geometry, having a discharge coefficient of 1.

The type of rupture is defined by partial (10%) rupture and total rupture 100% of the diameter of the pipe.

- Diameter of pools

The maximum size of the pool has been calculated to estimate the maximum extent of the spill that from the quantity of the leakage and considering an average thickness of the spill.

- Emission sources

There are two possible types of emission sources in all cases of vapor dispersion from a pool of liquid leakage:

Large Source: Homogeneous vaporization from the entire surface of the spill.

Point source: Emission from any point of spill which vaporizes the entire flow.

While the first, more realistic option describes the phenomenon, the second option is considered more preventive for considering possible point accumulations and establishing more conservative risk areas.

- Atmosphere stability

Stability B and D have been considered in all cases, being the most likely kind of stability and the most restrictive class of stability, respectively, providing the most conservative estimates to be the most stable class.

- Leak times

According REFERENCE MANUAL BEVI the leakages times are the following:

30 minutes for systems where automatic detection but manual intervention is required to activate a cutting system to stop the leak.

10 minutes for semi-automatic locking system where the fault is detected automatically Control Center and the court system can be activated by remote actuation of an operator from the center.

2 minutes for detection systems and fully automatic cutting. Or for systems where an operator is present permanently (eg during a tanker discharge operation) and there is also an emergency stop button nearby and the operator has received specific training with instructions for action.

In addition to these more general assumptions in each scenario calculation corresponding consequences particular hypothesis explains the developed sections detailing aspects such as leakage times used, etc.

- Weather conditions

Wind speed:

Annual average speed	3,42 m/s
Predominant direction	N
Temperature: Average temperature	15,5ºC
Relative humidity: Average relative humidity	72%
Pasquill stability class table	B and D
Terrain roughness class	1 m

- Software used to perfom consequences models

The software used for performing the calculation of consequences is EFFECTS 7.4 software by TNO.

- Consequences model of unloading tank module

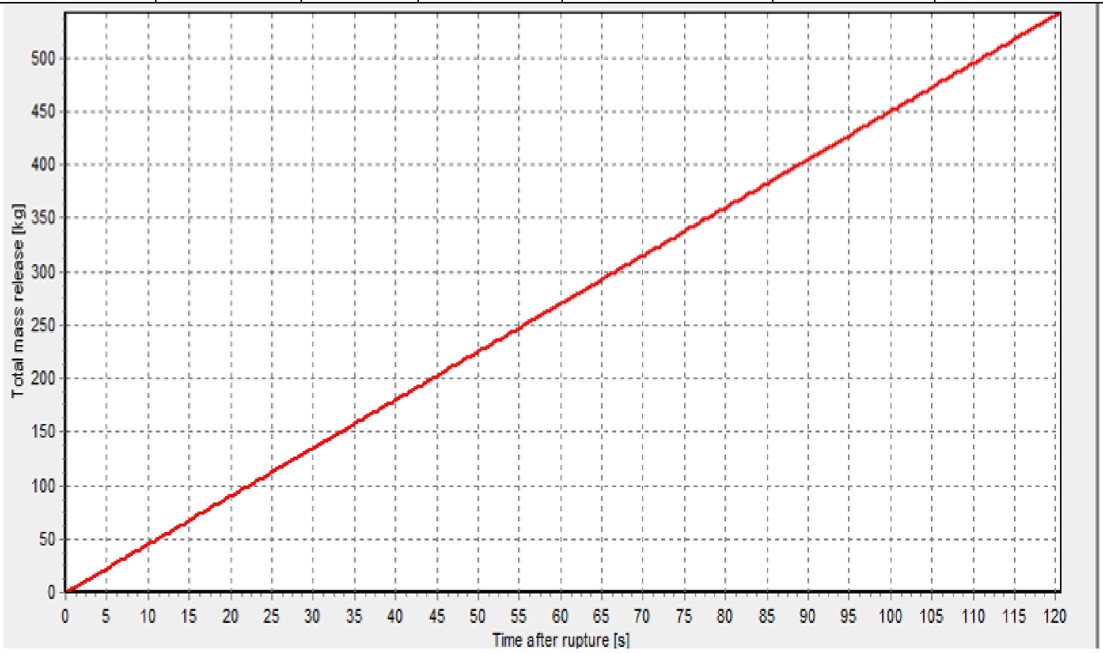
Table.6.5. Rupture of unloading LNG hose– HOS.1

Rupture of the flexible (3 '') for liquid phase discharge tank truck. Process parameters are the maximum service of LNG unloading operation; these provide by the cryogenic pump truck. The LNG unloading operation is supervised by the operator.			
Temperature (ºC)	-160	**Wind speed (m/s)**	3,42
Pressure (kPa)	500	**Temperature (ºC)**	15,5
Tank capacity (m^3)	40	**Humidity relative (%)**	72
Filling degree (%)	95	**Stability**	B & D

The basis for calculating time is 120 seconds as it is a supervised operation.

The flow rate is obtained by the maximum flow of the cryogenic pump truck. This provides 600 l/min (LNG density 0.45 kg / l). The leakage time, being a supervised operation, is done in 120 seconds.

Hose diameter (mm)	**Rupture type (%)**	**Phase**		**Average mass flow (kg/s)**	**Time (s)**	**Total mass release at 120s (kg)**
		L (%)	**V (%)**			
80	100 %	100	0	4,5	120	542

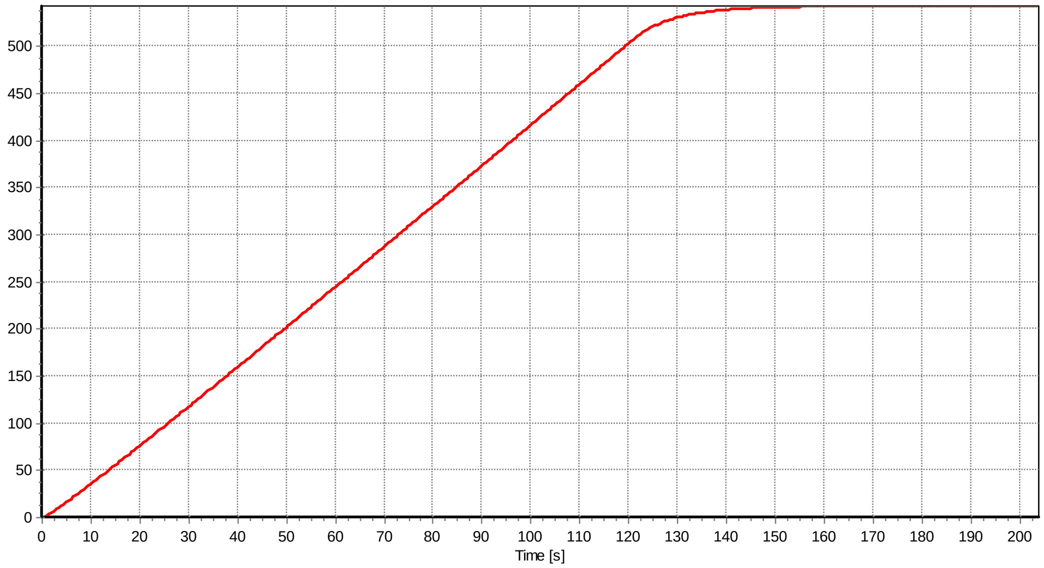


Total mass release Vs Time

A leak occurs for 120 s in liquid phase, forming pool evaporation. For further calculations the maximum values of "maximum radius of the spill" and "maximum rate of evaporation" are caught.

Total mass release at 120s (kg)	**Duration Evaporation Time (s)**	**Spill**		**Max evaporation rate (kg/s)**
		Max radius (m)	**Max Area (m^2)**	
542,5	204 (1)	2,35	17,3 (2)	4,32

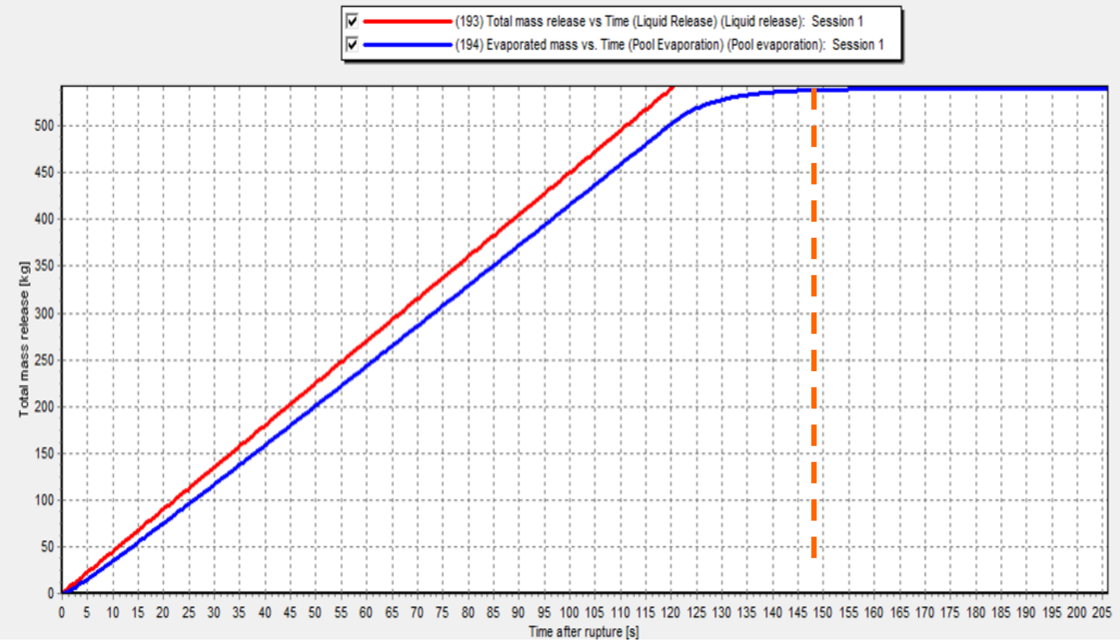
1. Until complete evaporation of all the leaked substance (includes leakage time 120 s)
2. Assuming a circular spill.



Evaporated mass Vs Time

In the graph presented below, the mass leakage (120 s) is compared to the evaporated mass. As can be seen, due to the characteristics of LNG, virtually liquid pool is no generated on the ground, as it evaporates almost immediately (in 120 s, evaporated 510 to 540 kg leakage).

Therefore, performing a calculation for an accident consequences associated with a Pool FIRE has been discarded.



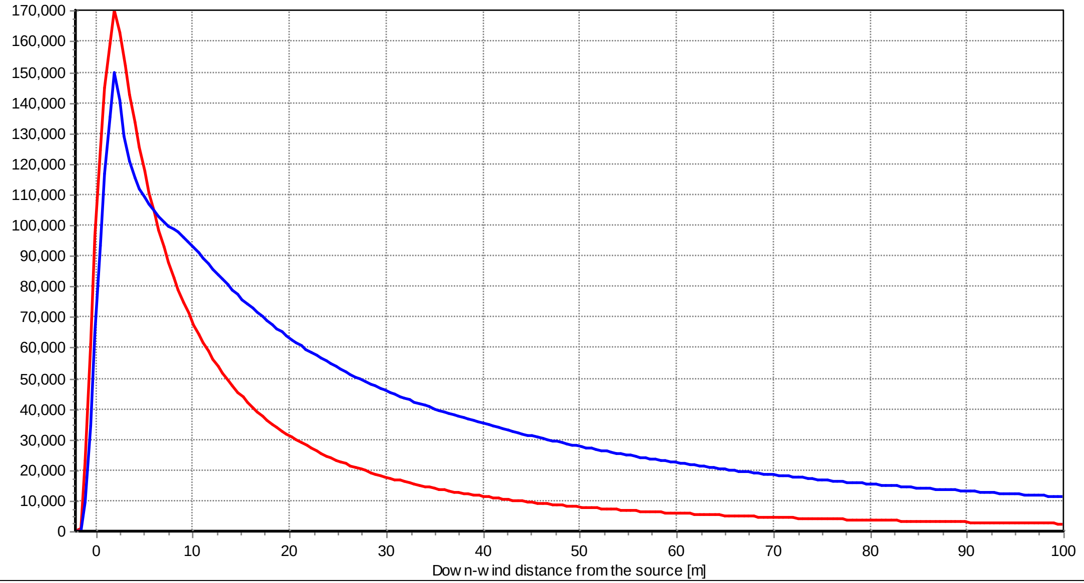
Stop leakage LNG at 120 s

To model the dispersion, the maximum value of the rate of evaporation is measured during the 204 seconds of the escape + evaporation. Resulting evaporation values, once the leakage is resolved, have been discarded because from that moment the evaporation rate is lower.

Dense gas model is utilized, since the natural gas at this temperature is denser than air. In the first instance the risk of explosion is studied.

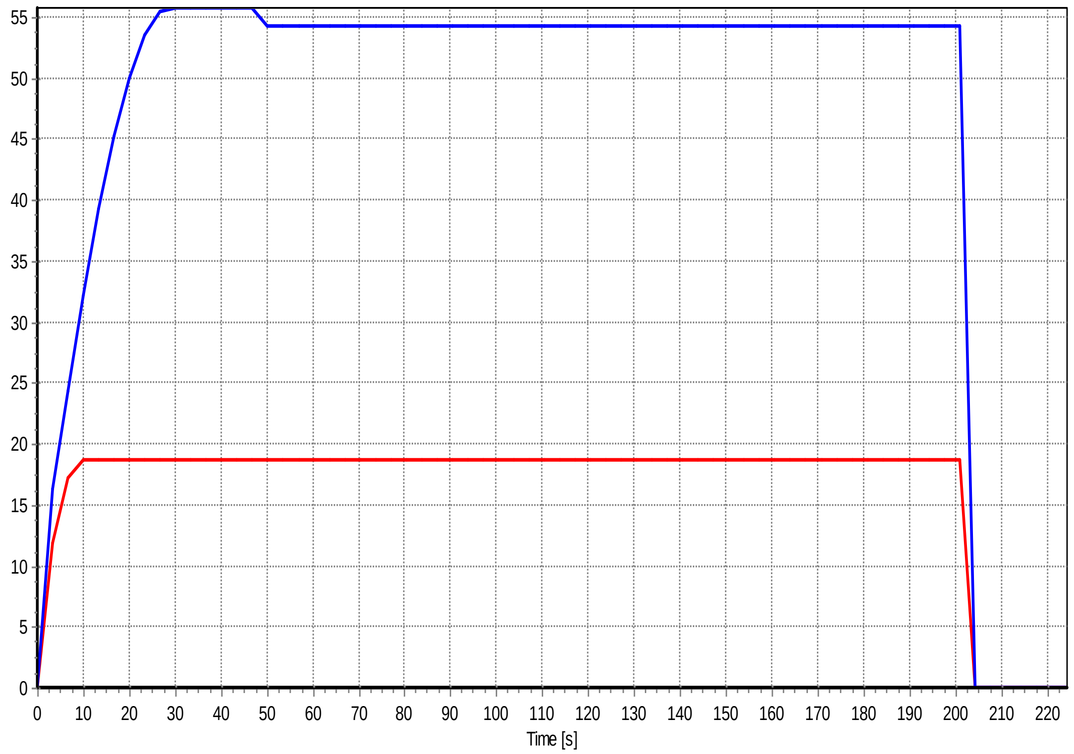
In order to do this, the maximum quantity of GN that can cause an explosion (LEL= 33353 mg / m^3 and the LSE=100700 mg / m^3 of natural gas of the cloud formed between the LEL - LSE concentration) was first studied in the cloud (both stability B and D). Then consequences of this explosion are calculated taking into account that being an unconfined explosion (UVCE), not all natural gas in the explosive range is effective in the explosion, only the percentage of it that is capable of "confinement ". Given the emission source and ground situation, the value of confinement is 10%.

Total mass release (kg)	**LIE (mg/m^3)**		**LSE (mg/m^3)**	
542,5	33353		100700	
Max evaporation rate (kg/s)	**Distance to LIE (m)**		**Distance to LSE (m)**	
4,32	**B**	**D**	**B**	**D**
	19	42	6	7



Concentration Vs Down-wind distance (stability class B –red- and D – blue-)

Cloud explosive dimensions					
Maximum quantity of substance in explosive range (kg)		**Max. explosive cloud area (m^2)**		**Time to reach maximum explosive cloud (s)**	
B	**D**	**B**	**D**	**B**	**D**
19	56	117	379	8	23

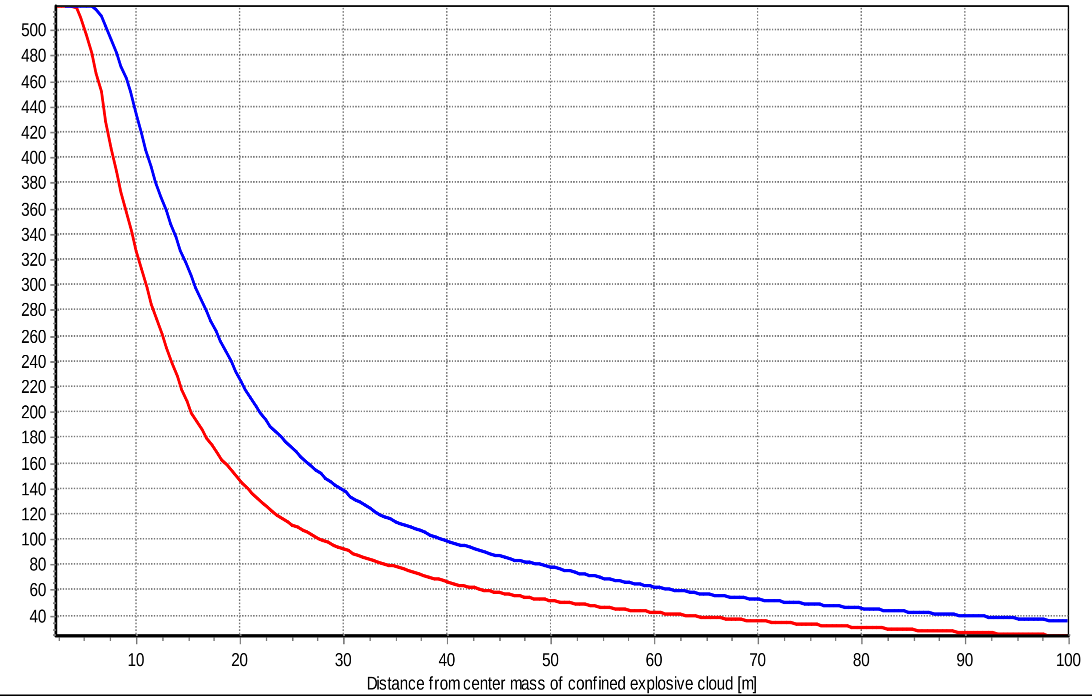


Explosive mass (kg) Vs Time (s) (stability class B –red- and D – blue-)

Explosive consequences and threshold values

Alert Zone (m)		**Intervention Zone (m)**		**Domino Effect Zone (m)**	
Overpressure **50 mbar**		**Overpressure** **125 mbar**		**Overpressure** **160 mbar**	
B	**D**	**B**	**D**	**B**	**D**
51	74	23	32	18	26
Impulse **100 mbar·sec**		**Impulse** **100 mbar·sec**		**Impulse** **---**	
B	**D**	**B**	**D**	**B**	**D**
N/A	N/A	N/A	N/A	N/A	N/A

Planning zones calculated by overpressure originating at the center of the explosive cloud.

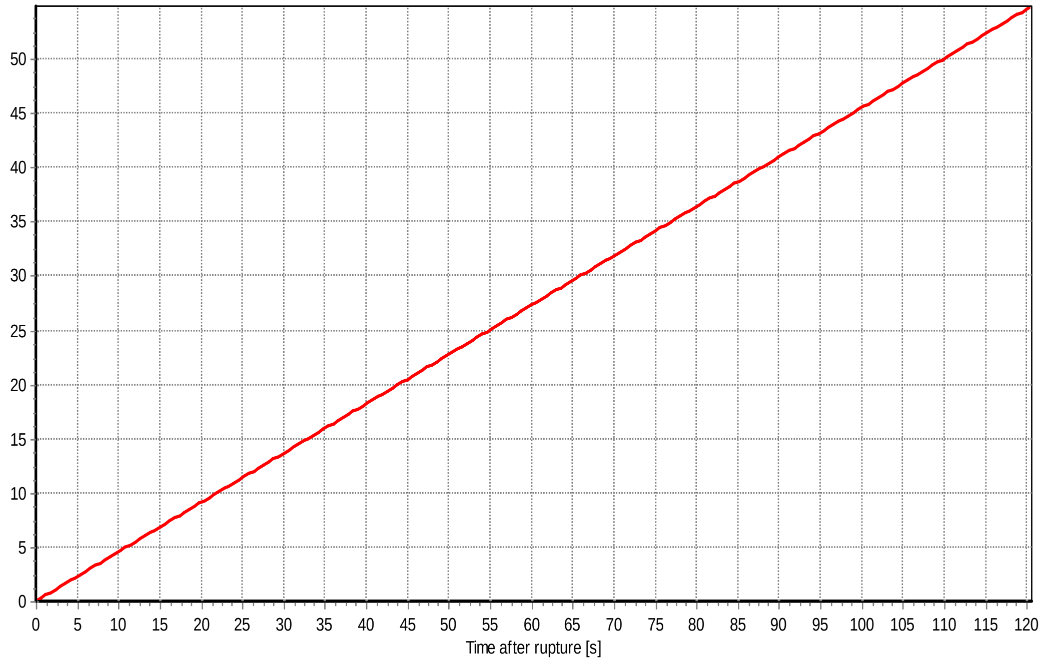


Overpressure (mbar) Vs Distance from center mass of confined explosive cloud(m) (stability class B –red- and D – blue)

Table.6.7. Leak in unloading LNG hose with an effective diameter of 10% of the nominal diameter – HOS.2

Leak (10%) of the flexible (3 '') for liquid phase discharge tank truck. Process parameters are the maximum service of LNG unloading operation, these provided by the cryogenic pump truck. The LNG unloading operation is supervised by the operator.			
Temperature (ºC)	-160	**Temperature (ºC)**	-160
Pressure (kPa)	500	**Pressure (kPa)**	500
Tank capacity (m^3)	40	**Tank capacity (m^3)**	40
Filling degree (%)	95	**Filling degree (%)**	95
The basis for calculating time is 120 seconds as it is a supervised operation. The flow rate is obtained by the maximum flow of the cryogenic pump truck. This provides 600 l/min (LNG density 0.45 kg / l). The leakage time, being a supervised operation, is done in 120 seconds.			

Hose diameter (mm)	**Rupture type (%)**	**Phase**		**Average mass flow (kg/s)**	**Time (s)**	**Total mass release at 120s (kg)**
		L (%)	**V (%)**			
80	10 %	100	0	0,45	120	54,8

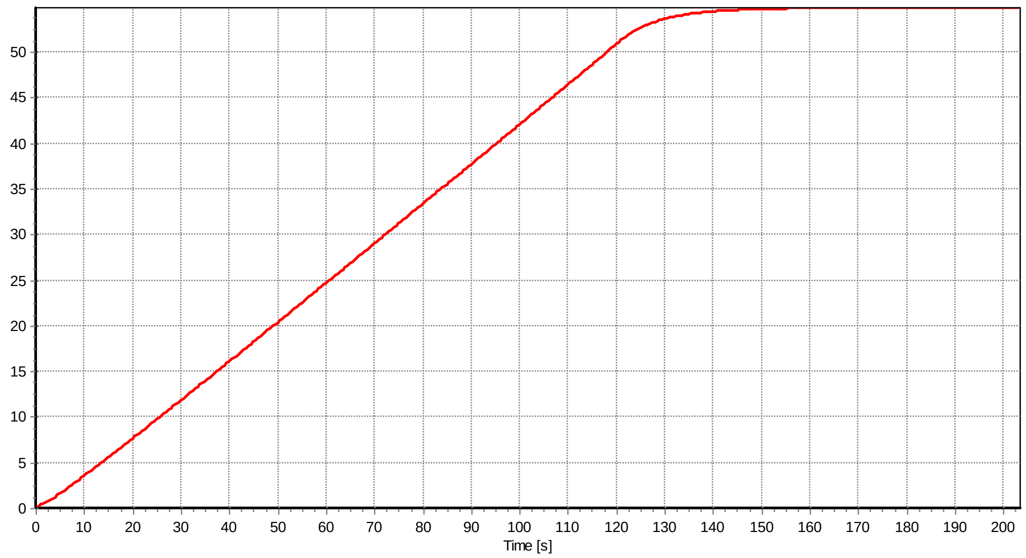


Total mass release Vs Time after rupture

A leak occurs for 120 s in liquid state, forming pool evaporation. For further calculations the maximum values of "maximum radius of the spill" and "maximum rate of evaporation" are caught.

Total mass release at 120s (kg)	**Duration Evaporation Time (s)**	**Spill**		**Max evaporation rate (kg/s)**
		Max radius (m)	**Max radius (m)**	
54,8	204 (1)	0,7	1,8 (2)	0,45

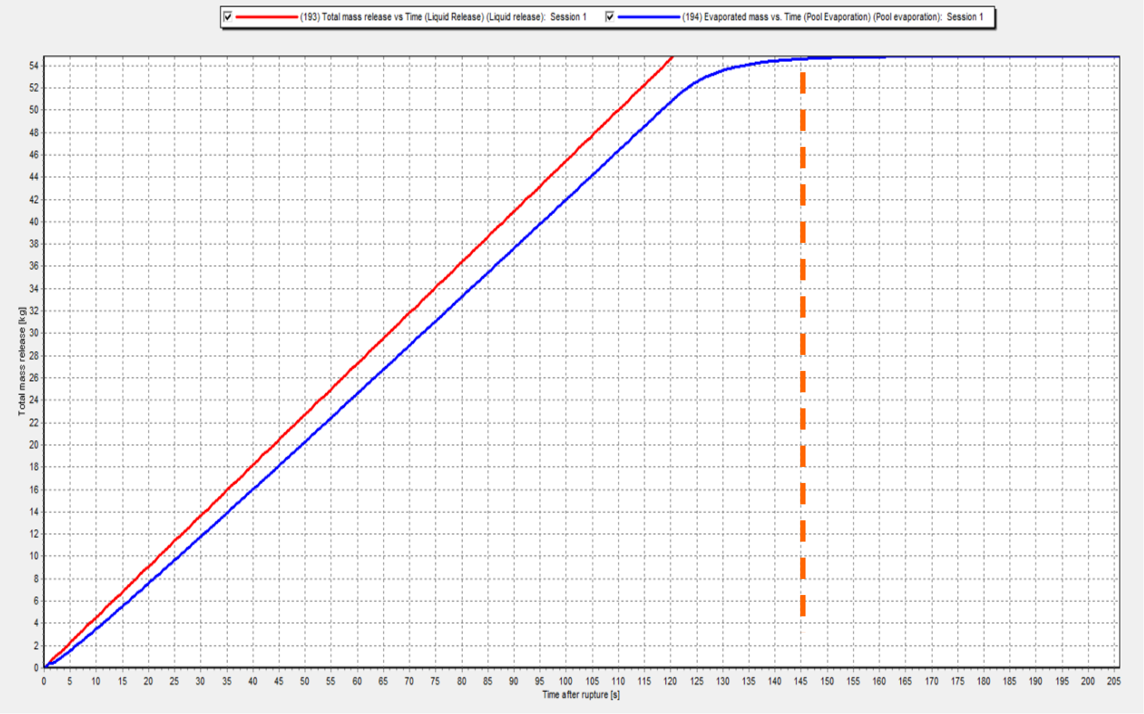
1. Until complete evaporation of all the leaked substance (includes leakage time -120 s)
2. Assuming a circular spill.



Evaporate mass Vs Time

In the graph presented below, the leaked amount (120 s) with the evaporated amount is compared to evaporated mass. As can be seen, due to the characteristics of LNG, virtually liquid pool is no generated on the ground, as it evaporates almost immediately (in 120 s, evaporated 51 de los 54,8 kg leakage).

Therefore performing a calculation for an accident consequences associated with a Pool FIRE has been discarded.



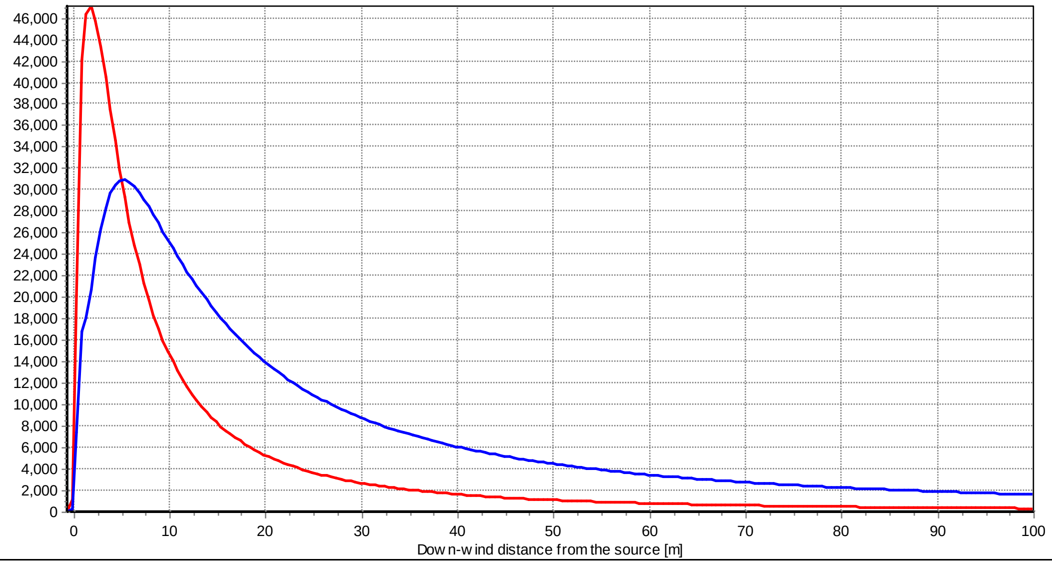
Stop leakage LNG at 120 s

To model the dispersion, the maximum value of the rate of evaporation is measured during the 206 seconds of the escape + evaporation. Resulting evaporation values, once the leakage is resolved, have been discarded because from that moment the evaporation rate is lower.

Dense gas model is utilized, since the natural gas at this temperature is denser than air. In the first instance the risk of explosion is studied.

In order to do this, the maximum quantity of GN that can cause an explosion (LEL 33353 mg / m3 and the LSE 100700 mg / m3 of natural gas of the cloud formed between the LEL - LSE concentration) was first studied in the cloud (both stability B and D). Then consequences of this explosion are calculated taking into account that being an unconfined explosion (UVCE), not all natural gas in the explosive range is effective in the explosion, only the percentage of it that is capable of "confinement ". Given the emission source and ground situation, the value of confinement is 10%.

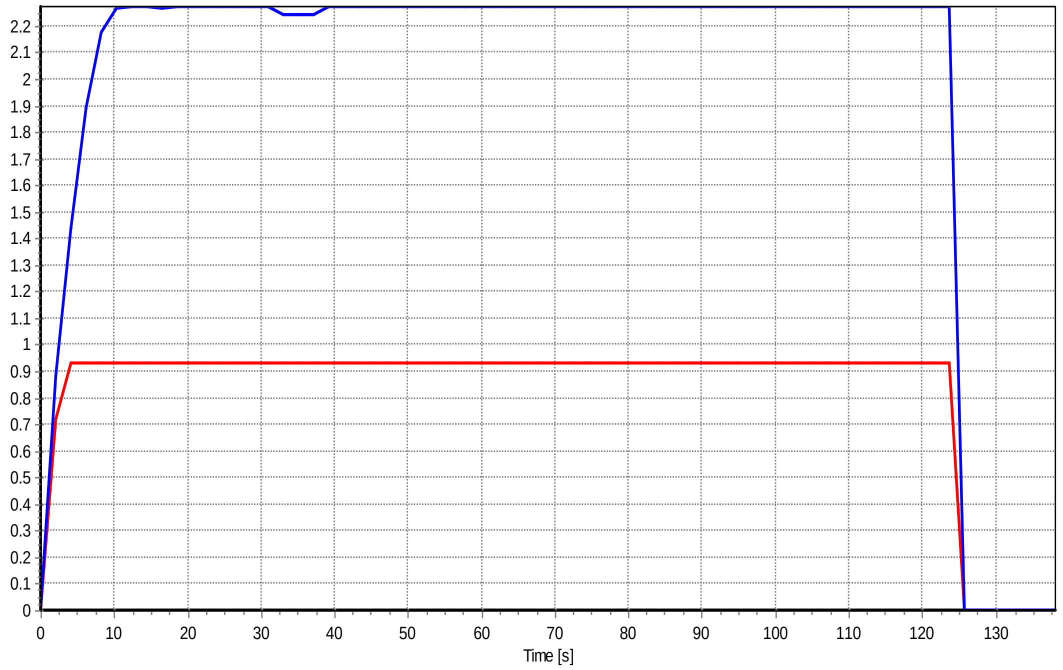
Total mass release (kg)	**LIE (mg/m^3)**		**LSE (mg/m^3)**	
54,8	33353		100700	
Max evaporation rate (kg/s)	**Distance to LIE (m)**		**Distance to LSE (m)**	
0,45	**B**	**D**	**B**	**D**
	4,5	--	Not achieved	

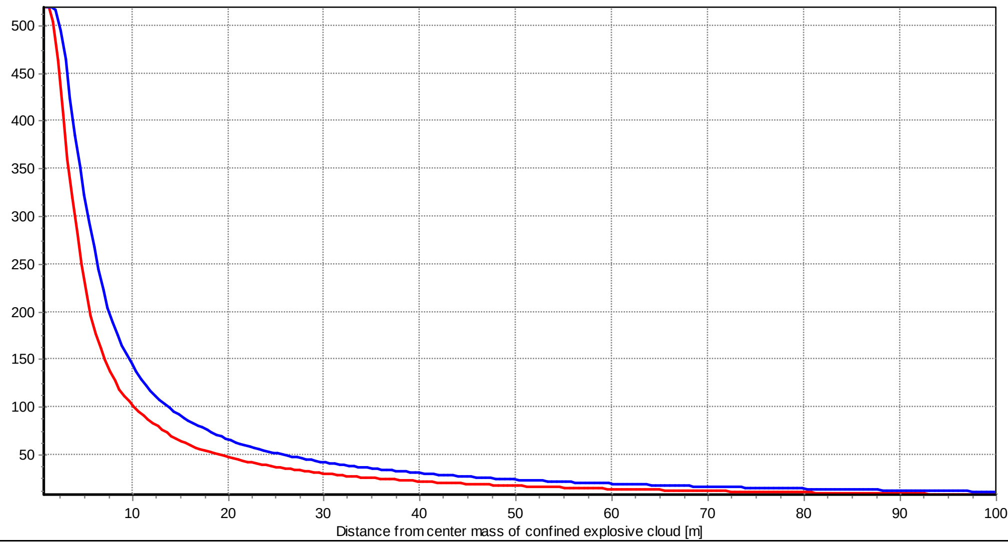


Concentration Vs Down-wind distance (stability class B –red- and D – blue-)

Cloud explosive dimensions

Maximum quantity of substance in explosive range (kg)	**Max. explosive cloud area (m^2)**	**Time to achieve maximum explosive cloud (s)**

B	D	B	D	B	D
0,9	2,3	11.7	31.7	3,6	8,1
					
Explosive mass (kg) Vs Time (s) (stability class B –red- and D – blue-)					
Explosive consequences and threshold values					
Alert Zone (m)		**Intervention Zone (m)**		**Domino Effect Zone (m)**	
Overpressure **50 mbar**		**Overpressure** **125 mbar**		**Overpressure** **160 mbar**	
B	**D**	**B**	**D**	**B**	**D**
19	25	8	11	7	9
Impulse **100 mbar·seg**		**Impulse** **100 mbar·seg**		**Impulse** ---	
B	**D**	**B**	**D**	**B**	**D**
N/A	N/A	N/A	N/A	N/A	N/A
Planning zones calculated by overpressure originating at the center of the explosive cloud.					



Overpressure (mbar) Vs Distance from center mass of confined explosive cloud (m) (stability class B –red- and D – blue)

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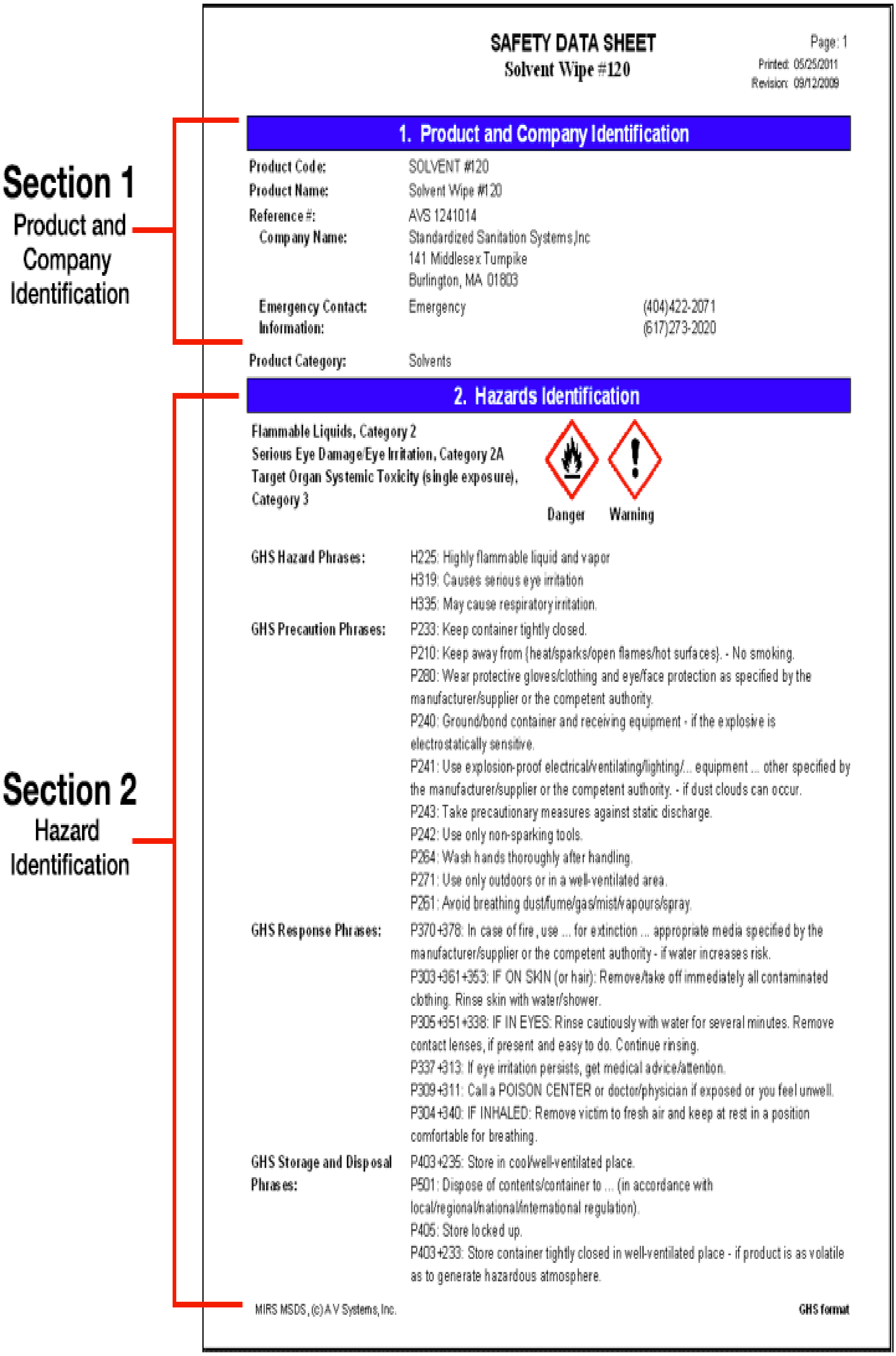
ANNEXES

ANNEX A



SAFETY DATA SHEET
Solvent Wipe #120

Page: 1
Printed: 05/25/2011
Revision: 09/12/2009

1. Product and Company Identification

Product Code:	SOLVENT #120	
Product Name:	Solvent Wipe #120	
Reference #:	AVS 1241014	
Company Name:	Standardized Sanitation Systems,Inc 141 Middlesex Turnpike Burlington, MA 01803	
Emergency Contact: Information:	Emergency	(404)422-2071 (617)273-2020
Product Category:	Solvents	

2. Hazards Identification

Flammable Liquids, Category 2
Serious Eye Damage/Eye Irritation, Category 2A
Target Organ Systemic Toxicity (single exposure), Category 3

GHS Hazard Phrases:
H225: Highly flammable liquid and vapor
H319: Causes serious eye irritation
H335: May cause respiratory irritation.

GHS Precaution Phrases:
P233: Keep container tightly closed.
P210: Keep away from {heat/sparks/open flames/hot surfaces}. - No smoking.
P280: Wear protective gloves/clothing and eye/face protection as specified by the manufacturer/supplier or the competent authority.
P240: Ground/bond container and receiving equipment - if the explosive is electrostatically sensitive.
P241: Use explosion-proof electrical/ventilating/lighting/... equipment ... other specified by the manufacturer/supplier or the competent authority. - if dust clouds can occur.
P243: Take precautionary measures against static discharge.
P242: Use only non-sparking tools.
P264: Wash hands thoroughly after handling.
P271: Use only outdoors or in a well-ventilated area.
P261: Avoid breathing dust/fume/gas/mist/vapours/spray.

GHS Response Phrases:
P370+378: In case of fire , use ... for extinction ... appropriate media specified by the manufacturer/supplier or the competent authority - if water increases risk.
P303+361+353: IF ON SKIN (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower.
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P337+313: If eye irritation persists, get medical advice/attention.
P309+311: Call a POISON CENTER or doctor/physician if exposed or you feel unwell.
P304+340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.

GHS Storage and Disposal Phrases:
P403+235: Store in cool/well-ventilated place.
P501: Dispose of contents/container to ... (in accordance with local/regional/national/international regulation).
P405: Store locked up.
P403+233: Store container tightly closed in well-ventilated place - if product is as volatile as to generate hazardous atmosphere.

MIRS MSDS, (c) A V Systems, Inc. **GHS format**

ANNEXB

MATERIAL SAFETY DATA SHEET — 16 Sections

SECTION 1 — CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Identifier			[WHMIS Classification]
Product Use			
Manufacturer's Name		Supplier's Name	
Street Address		Street Address	
City	Province	City	Province
Postal Code	Emergency Telephone	Postal Code	Emergency Telephone
Date MSDS Prepared	MSDS Prepared By	Phone Number	

SECTION 2 — COMPOSITION/INFORMATION ON INGREDIENTS

Hazardous Ingredients *(specific)*	%	CAS Number	LD_{50} of Ingredient *(specify species and route)*	LC_{50} of Ingredient *(specify species)*

SECTION 3 — HAZARDS IDENTIFICATION

Route of Entry ☐ Skin Contact ☐ Skin Absorption ☐ Eye Contact ☐ Inhalation ☐ Ingestion

[Emergency Overview]

[WHMIS Symbols]

[Potential Health Effects]

SECTION 4 — FIRST AID MEASURES

Skin Contact

Eye Contact

Inhalation

Ingestion

SAMPLE FORMAT PROVIDED BY THE WORKERS' COMPENSATION BOARD OF BRITISH COLUMBIA

57M6 (6/99)

Please continue on reverse side

[Optional, not required under WHMIS]

SECTION 5 — FIRE FIGHTING MEASURES

Flammable ☐ Yes ☐ No	If yes, under which conditions?	
Means of Extinction		
Flashpoint (°C) and Method	Upper Flammable Limit (% by volume)	Lower Flammable Limit (% by volume)
Autoignition Temperature (°C)	Explosion Data – Sensitivity to Impact	Explosion Data – Sensitivity to Static Discharge
Hazardous Combustion Products		
[NFPA]		

SECTION 6 — ACCIDENTAL RELEASE MEASURES

Leak and Spill Procedures

SECTION 7 — HANDLING AND STORAGE

Handling Procedures and Equipment
Storage Requirements

SECTION 8 — EXPOSURE CONTROL / PERSONAL PROTECTION

Exposure Limits	☐ ACGIH TLV	☐ OSHA PEL	☐ Other *(specify)*			
Specific Engineering Controls *(such as ventilation, enclosed process)*						
Personal Protective Equipment	☐ Gloves	☐ Respirator	☐ Eye	☐ Footwear	☐ Clothing	☐ Other
If checked, please specify type						

[Optional, not required under WHMIS]

Product Identifier

SECTION 9 — PHYSICAL AND CHEMICAL PROPERTIES

Physical State	Odour and Appearance	Odour Threshold (ppm)
Specific Gravity	Vapour Density (air = 1)	Vapour Pressure (mmHg)
Evaporation Rate	Boiling Point (°C)	Freezing Point (°C)
pH	Coefficient of Water/Oil Distribution	[Solubility in Water]

SECTION 10 — STABILITY AND REACTIVITY

Chemical Stability ☐ Yes ☐ No	If no, under which conditions?
Incompatibility with Other Substances ☐ Yes ☐ No	If yes, which ones?
Reactivity, and under what conditions?	
Hazardous Decomposition Products	

SECTION 11 — TOXICOLOGICAL INFORMATION

Effects of Acute Exposure	
Effects of Chronic Exposure	
Irritancy of Product	
Skin Sensitization	Respiratory Sensitization
Carcinogenicity – IARC	Carcinogenicity – ACGIH
Reproductive Toxicity	Teratogenicity
Embryotoxicity	Mutagenicity
Name of Synergistic Products/Effects	

[Optional, not required under WHMIS]

Please continue on reverse side

Product Identifier

SECTION 12 — ECOLOGICAL INFORMATION

[Aquatic Toxicity]

SECTION 13 — DISPOSAL CONSIDERATIONS

Waste Disposal

SECTION 14 — TRANSPORT INFORMATION

Special Shipping Information

PIN

TDG	[DOT]
[IMO]	[ICAO]

SECTION 15 — REGULATORY INFORMATION

[WHMIS Classification]	[OSHA]
[SERA]	[TSCA]

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by CPR.

SECTION 16 — OTHER INFORMATION

[Optional, not required under WHMIS]

ANNEX C

CANDIDATE LIST*

The name of Substance	EC No.	CAS No	Date of inclusion
4,4'-isopropylidenediphenol (bisphenol A; BPA)	201-245-8	80-05-7	2017/01/12
4-Heptylphenol, branched and linear	-	-	2017/01/12
Nonadecafluorodecanoic acid (PFDA) and its sodium and ammonium salts	-	-	2017/01/12
p-(1,1-dimethylpropyl)phenol	201-280-9	80-46-6	2017/01/12
Benzo[def]chrysene (Benzo[a]pyrene)	200-028-5	50-32-8	2016/06/20
1,3-propanesultone	214-317-9	1120-71-4	2015/12/17
2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol (UV-327)	223-383-8	3864-99-1	2015/12/17
2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol (UV-350)	253-037-1	36437-37-3	2015/12/17
Nitrobenzene	202-716-0	98-95-3	2015/12/17
Perfluorononan-1-oic-acid and its sodium and ammonium salts	206-801-3	375-95-1 21049-39-8 4149-60-4	2015/12/17
1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters; 1,2-benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters with ≥ 0.3% of dihexyl phthalate (EC No. 201-559-5)	271-094-0 272-013-1	68515-51-5 68648-93-1	2015/06/15
5-sec-butyl-2-(2,4-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane [1], 5-sec-butyl-2-(4,6-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane [2] [covering any of the individual stereoisomers of [1] and [2] or any combination thereof]	-	-	2015/06/15
Bis (2-ethylhexyl)phthalate (DEHP)	204-211-0	117-81-7	2014/12/17; 2008/10/28
2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)	247-384-8	25973-55-1	2014/12/17
2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)	223-346-6	3846-71-7	2014/12/17
2-ethylhexyl 10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate (DOTE)	239-622-4	15571-58-1	2014/12/17
Cadmium fluoride	232-222-0	7790-79-6	2014/12/17
Cadmium sulphate	233-331-6	10124-36-4 31119-53-6	2014/12/17
reaction mass of 2-ethylhexyl 10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate and 2-ethylhexyl 10-ethyl-4-[[2-[(2-ethylhexyl)oxy]-2-oxoethyl]thio]-4-octyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate (reaction mass of DOTE and MOTE)	-	-	2014/12/17
1,2-Benzenedicarboxylic acid, dihexylester, branched and linear	271-093-5	68515-50-4	2014/06/16
Cadmium chloride	233-296-7	10108-64-2	2014/06/16
Sodium perborate,perboric acid, sodium salt	239-172-9 234-390-0	-	2014/06/16
Sodium peroxometaborate	231-556-4	7632-04-4	2014/06/16
Cadmium sulphide	215-147-8	1306-23-6	2013/12/16
Dihexyl phthalate	201-559-5	84-75-3	2013/12/16
Disodium 3,3'-[[1,1'-biphenyl]-4,4'-diylbis(azo)]bis(4-aminonaphthalene-1-sulphonate) (C.I. Direct Red 28)	209-358-4	573-58-0	2013/12/16

Disodium 4-amino-3-[[4'-[(2,4-diaminophenyl)azo][1,1'-biphenyl]-4-yl]azo] -5-hydroxy-6-(phenylazo)naphthalene-2,7-disulphonate (C.I. Direct Black 38)	217-710-3	1937-37-7	2013/12/16
Imidazolidine-2-thione (2-imidazoline-2-thiol)	202-506-9	96-45-7	2013/12/16
Lead di(acetate)	206-104-4	301-04-2	2013/12/16
Trixylyl phosphate	246-677-8	25155-23-1	2013/12/16
4-Nonylphenol, branched and linear, ethoxylated [substances with a linear and/or branched alkyl chain with a carbon number of 9 covalently bound in position 4 to phenol, ethoxylated covering UVCB- and well-defined substances, polymers and homologues, which include any of the individual isomers and/or combinations thereof]	-	-	2013/06/20
Ammonium pentadecafluorooctanoate (APFO)	223-320-4	3825-26-1	2013/06/20
Cadmium	231-152-8	7440-43-9	2013/06/20
Cadmium oxide	215-146-2	1306-19-0	2013/06/20
Dipentyl phthalate (DPP)	205-017-9	131-18-0	2013/06/20
Pentadecafluorooctanoic acid (PFOA)	206-397-9	335-67-1	2013/06/20
1,2-Benzenedicarboxylic acid, dipentylester, branched and linear	284-032-2	84777-06-0	2012/12/19
1,2-Diethoxyethane	211-076-1	629-14-1	2012/12/19
1-bromopropane (n-propyl bromide)	203-445-0	106-94-5	2012/12/19
3-ethyl-2-methyl-2-(3-methylbutyl)-1,3-oxazolidine	421-150-7	143860-04-2	2012/12/19
4,4'-methylenedi-o-toluidine	212-658-8	838-88-0	2012/12/19
4,4'-oxydianiline and its salts	202-977-0	101-80-4	2012/12/19
4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated [covering well-defined substances and UVCB substances, polymers and homologues]	-	-	2012/12/19
4-Aminoazobenzene	200-453-6	60-09-3	2012/12/19
4-methyl-m-phenylenediamine (toluene-2,4-diamine)	202-453-1	95-80-7	2012/12/19
4-Nonylphenol, branched and linear [substances with a linear and/or branched alkyl chain with a carbon number of 9 covalently bound in position 4 to phenol, covering also UVCB- and well-defined substances which include any of the individual isomers or a combination thereof]	-	-	2012/12/19
6-methoxy-m-toluidine (p-cresidine)	204-419-1	120-71-8	2012/12/19
[Phthalato(2-)]dioxotrilead	273-688-5	69011-06-9	2012/12/19
Acetic acid, lead salt, basic	257-175-3	51404-69-4	2012/12/19
Biphenyl-4-ylamine	202-177-1	92-67-1	2012/12/19
Bis(pentabromophenyl) ether (decabromodiphenyl ether) (DecaBDE)	214-604-9	1163-19-5	2012/12/19
Cyclohexane-1,2-dicarboxylic anhydride [1], cis-cyclohexane-1,2-dicarboxylic anhydride [2], trans-cyclohexane-1,2-dicarboxylic anhydride [3] [The individual cis- [2] and trans- [3] isomer substances and all possible combinations of the cis- and trans-isomers [1] are covered by this entry]	201-604-9 236-086-3 238-009-9	85-42-7 13149-00-3 14166-21-3	2012/12/19
Diazene-1,2-dicarboxamide (C,C`-azodi(formamide)) (ADCA)	204-650-8	123-77-3	2012/12/19
Dibutyltin dichloride (DBTC)	211-670-0	683-18-1	2012/12/19
Diethyl sulphate	200-589-6	64-67-5	2012/12/19
Diisopentylphthalate	210-088-4	605-50-5	2012/12/19
Dimethyl sulphate	201-058-1	77-78-1	2012/12/19
Dinoseb (6-sec-butyl-2,4-dinitrophenol)	201-861-7	88-85-7	2012/12/19

Dioxobis(stearato)trilead	235-702-8	12578-12-0	2012/12/19
Fatty acids, C16-18, lead salts	292-966-7	91031-62-8	2012/12/19
Furan	203-727-3	110-00-9	2012/12/19
Henicosafluoroundecanoic acid	218-165-4	2058-94-8	2012/12/19
Heptacosafluorotetradecanoic acid	206-803-4	376-06-7	2012/12/19
Hexahydromethylphthalic anhydride [1], Hexahydro-4-methylphthalic anhydride [2], Hexahydro-1-methylphthalic anhydride [3], Hexahydro-3-methylphthalic anhydride [4] [The individual isomers [2], [3] and [4] (including their cis- and trans- stereo isomeric forms) and all possible combinations of the isomers [1] are covered by this entry]	247-094-1 243-072-0 256-356-4 260-566-1	25550-51-0 19438-60-9 48122-14-1 57110-29-9	2012/12/19
Lead bis(tetrafluoroborate)	237-486-0	13814-96-5	2012/12/19
Lead cyanamidate	244-073-9	20837-86-9	2012/12/19
Lead dinitrate	233-245-9	10099-74-8	2012/12/19
Lead monoxide (lead oxide)	215-267-0	1317-36-8	2012/12/19
Lead oxide sulfate	234-853-7	12036-76-9	2012/12/19
Lead titanium trioxide	235-038-9	12060-00-3	2012/12/19
Lead titanium zirconium oxide	235-727-4	12626-81-2	2012/12/19
Methoxyacetic acid	210-894-6	625-45-6	2012/12/19
Methyloxirane (Propylene oxide)	200-879-2	75-56-9	2012/12/19
N,N-dimethylformamide	200-679-5	68-12-2	2012/12/19
N-methylacetamide	201-182-6	79-16-3	2012/12/19
N-pentyl-isopentylphthalate	-	776297-69-9	2012/12/19
o-aminoazotoluene	202-591-2	97-56-3	2012/12/19
o-Toluidine	202-429-0	95-53-4	2012/12/19
Orange lead (lead tetroxide)	215-235-6	1314-41-6	2012/12/19
Pentacosafluorotridecanoic acid	276-745-2	72629-94-8	2012/12/19
Pentalead tetraoxide sulphate	235-067-7	12065-90-6	2012/12/19
Pyrochlore, antimony lead yellow	232-382-1	8012-00-8	2012/12/19
Silicic acid (H2Si2O5), barium salt (1:1), lead-doped [with lead (Pb) content above the applicable generic concentration limit for ’toxicity for reproduction’ Repr. 1A (CLP) or category 1 (DSD),the substance is a member of the group entry of lead compounds, with index number 082-001-00-6 in Regulation (EC) No 1272/2008]	272-271-5	68784-75-8	2012/12/19
Silicic acid, lead salt	234-363-3	11120-22-2	2012/12/19
Sulfurous acid, lead salt, dibasic	263-467-1	62229-08-7	2012/12/19
Tetraethyllead	201-075-4	78-00-2	2012/12/19
Tetralead trioxide sulphate	235-380-9	12202-17-4	2012/12/19
Tricosafluorododecanoic acid	206-203-2	307-55-1	2012/12/19
Trilead bis(carbonate) dihydroxide	215-290-6	1319-46-6	2012/12/19
Trilead dioxide phosphonate	235-252-2	12141-20-7	2012/12/19
1,2-bis(2-methoxyethoxy)ethane (TEGDME,triglyme)	203-977-3	112-49-2	2012/06/18
1,2-dimethoxyethane,ethylene glycol dimethyl ether (EGDME)	203-794-9	110-71-4	2012/06/18
1,3,5-Tris(oxiran-2-ylmethyl)-1,3,5-triazinane-2,4,6-trione (TGIC)	219-514-3	2451-62-9	2012/06/18
1,3,5-tris[(2S and 2R)-2,3-epoxypropyl]-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (β-TGIC)	423-400-0	59653-74-6	2012/06/18

4,4'-bis(dimethylamino)-4"-(methylamino)trityl alcohol [with ≥ 0.1% of Michler's ketone (EC No. 202-027-5) or Michler's base (EC No. 202-959-2)]	209-218-2	561-41-1	2012/06/18
4,4'-bis(dimethylamino)benzophenone (Michler's ketone)	202-027-5	90-94-8	2012/06/18
[4-[4,4'-bis(dimethylamino) benzhydrylidene]cyclohexa-2,5-dien-1-ylidene]dimethylammonium chloride (C.I. Basic Violet 3) [with ≥ 0.1% of Michler's ketone (EC No. 202-027-5) or Michler's base (EC No. 202-959-2)]	208-953-6	548-62-9	2012/06/18
[4-[[4-anilino-1-naphthyl][4-(dimethylamino)phenyl]methylene]cyclohexa-2,5-dien-1-ylidene] dimethylammonium chloride (C.I. Basic Blue 26) [with ≥ 0.1% of Michler's ketone (EC No. 202-027-5) or Michler's base (EC No. 202-959-2)]	219-943-6	2580-56-5	2012/06/18
Diboron trioxide	215-125-8	1303-86-2	2012/06/18
Formamide	200-842-0	75-12-7	2012/06/18
Lead(II) bis(methanesulfonate)	401-750-5	17570-76-2	2012/06/18
N,N,N',N'-tetramethyl-4,4'-methylenedianiline (Michler's base)	202-959-2	101-61-1	2012/06/18
α,α-Bis[4-(dimethylamino)phenyl]-4 (phenylamino)naphthalene-1-methanol (C.I. Solvent Blue 4) [with ≥ 0.1% of Michler's ketone (EC No. 202-027-5) or Michler's base (EC No. 202-959-2)]	229-851-8	6786-83-0	2012/06/18
1,2-Dichloroethane	203-458-1	107-06-2	2011/12/19
2,2'-dichloro-4,4'-methylenedianiline	202-918-9	101-14-4	2011/12/19
2-Methoxyaniline,o-Anisidine	201-963-1	90-04-0	2011/12/19
4-(1,1,3,3-tetramethylbutyl)phenol	205-426-2	140-66-9	2011/12/19
Aluminosilicate Refractory Ceramic Fibres are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, and fulfil the three following conditions: a) oxides of aluminium and silicon are the main components present (in the fibres) within variable concentration ranges b) fibres have a length weighted geometric mean diameter less two standard geometric errors of 6 or less micrometres (μm) c) alkaline oxide and alkali earth oxide (Na2O+K2O+CaO+MgO+BaO) content less or equal to 18% by weight	-	-	2011/12/19
Arsenic acid	231-901-9	7778-39-4	2011/12/19
Bis(2-methoxyethyl) ether	203-924-4	111-96-6	2011/12/19
Bis(2-methoxyethyl) phthalate	204-212-6	117-82-8	2011/12/19
Calcium arsenate	231-904-5	7778-44-1	2011/12/19
Dichromium tris(chromate)	246-356-2	24613-89-6	2011/12/19
Formaldehyde, oligomeric reaction products with aniline	500-036-1	25214-70-4	2011/12/19
Lead diazide, Lead azide	236-542-1	13424-46-9	2011/12/19
Lead dipicrate	229-335-2	6477-64-1	2011/12/19
Lead styphnate	239-290-0	15245-44-0	2011/12/19
N,N-dimethylacetamide	204-826-4	127-19-5	2011/12/19
Pentazinc chromate octahydroxide	256-418-0	49663-84-5	2011/12/19
Phenolphthalein	201-004-7	77-09-8	2011/12/19
Potassium hydroxyoctaoxodizincatedichromate	234-329-8	11103-86-9	2011/12/19
Trilead diarsenate	222-979-5	3687-31-8	2011/12/19

Zirconia Aluminosilicate Refractory Ceramic Fibres are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, and fulfil the three following conditions: a) oxides of aluminium, silicon and zirconium are the main components present (in the fibres) within variable concentration ranges b) fibres have a length weighted geometric mean diameter less two standard geometric errors of 6 or less micrometres (µm). c) alkaline oxide and alkali earth oxide (Na2O+K2O+CaO+MgO+BaO) content less or equal to 18% by weight	-	-	2011/12/19
Cobalt dichloride	231-589-4	7646-79-9	2011/06/20 - 2008/10/28
1,2,3-trichloropropane	202-486-1	96-18-4	2011/06/20
1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich	276-158-1	71888-89-6	2011/06/20
1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters	271-084-6	68515-42-4	2011/06/20
1-Methyl-2-pyrrolidone (NMP)	212-828-1	872-50-4	2011/06/20
2-Ethoxyethyl acetate	203-839-2	111-15-9	2011/06/20
Hydrazine	206-114-9	302-01-2 7803-57-8	2011/06/20
Strontium chromate	232-142-6	7789-06-2	2011/06/20
2-Ethoxyethanol	203-804-1	110-80-5	2010/12/15
2-Methoxyethanol	203-713-7	109-86-4	2010/12/15
Acids generated from chromium trioxide and their oligomers. Names of the acids and their oligomers: Chromic acid, Dichromic acid, Oligomers of chromic acid and dichromic acid.	231-801-5 236-881-5	7738-94-5 13530-68-2	2010/12/15
Chromium trioxide	215-607-8	1333-82-0	2010/12/15
Cobalt(II) carbonate	208-169-4	513-79-1	2010/12/15
Cobalt(II) diacetate	200-755-8	71-48-7	2010/12/15
Cobalt(II) dinitrate	233-402-1	10141-05-6	2010/12/15
Cobalt(II) sulphate	233-334-2	10124-43-3	2010/12/15
Ammonium dichromate	232-143-1	7789-09-5	2010/06/18
Boric acid	233-139-2 234-343-4	10043-35-3 11113-50-1	2010/06/18
Disodium tetraborate, anhydrous	215-540-4	1303-96-4 1330-43-4 12179-04-3	2010/06/18
Potassium chromate	232-140-5	7789-00-6	2010/06/18
Potassium dichromate	231-906-6	7778-50-9	2010/06/18
Sodium chromate	231-889-5	7775-11-3	2010/06/18
Tetraboron disodium heptaoxide, hydrate	235-541-3	12267-73-1	2010/06/18
Trichloroethylene	201-167-4	79-01-6	2010/06/18
Acrylamide	201-173-7	79-06-1	2010/03/30
2,4-Dinitrotoluene	204-450-0	121-14-2	2010/01/13
Anthracene oil	292-602-7	90640-80-5	2010/01/13
Anthracene oil, anthracene paste	292-603-2	90640-81-6	2010/01/13
Anthracene oil, anthracene paste, anthracene fraction	295-275-9	91995-15-2	2010/01/13

Anthracene oil, anthracene paste, distn. lights	295-278-5	91995-17-4	2010/01/13
Anthracene oil, anthracene-low	292-604-8	90640-82-7	2010/01/13
Diisobutyl phthalate	201-553-2	84-69-5	2010/01/13
Lead chromate	231-846-0	7758-97-6	2010/01/13
Lead chromate molybdate sulphate red (C.I. Pigment Red 104)	235-759-9	12656-85-8	2010/01/13
Lead sulfochromate yellow (C.I. Pigment Yellow 34)	215-693-7	1344-37-2	2010/01/13
Pitch, coal tar, high temp.	266-028-2	65996-93-2	2010/01/13
Tris(2-chloroethyl)phosphate	204-118-5	115-96-8	2010/01/13
4,4'- Diaminodiphenylmethane (MDA)	202-974-4	101-77-9	2008/10/28
5-tert-butyl-2,4,6-trinitro-m-xylene (Musk xylene)	201-329-4	81-15-2	2008/10/28
Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins)	287-476-5	85535-84-8	2008/10/28
Anthracene	204-371-1	120-12-7	2008/10/28
Benzyl butyl phthalate (BBP)	201-622-7	85-68-7	2008/10/28
Bis(tributyltin) oxide (TBTO)	200-268-0	56-35-9	2008/10/28
Diarsenic pentaoxide	215-116-9	1303-28-2	2008/10/28
Diarsenic trioxide	215-481-4	1327-53-3	2008/10/28
Dibutyl phthalate (DBP)	201-557-4	84-74-2	2008/10/28
Hexabromocyclododecane (HBCDD) and all major diastereoisomers identified: Alpha-hexabromocyclododecane Beta-hexabromocyclododecane Gamma-hexabromocyclododecane	247-148-4 221-695-9	25637-99-4 3194-55-6 134237-50-6 134237-51-7 134237-52-8	2008/10/28
Lead hydrogen arsenate	232-064-2	7784-40-9	2008/10/28
Sodium dichromate	234-190-3	7789-12-0 10588-01-9	2008/10/28
Triethyl arsenate	427-700-2	15606-95-8	2008/10/28

***Last Updated on January 12, 2017**

(**for more information:**https://echa.europa.eu/candidate-list-table)

ANNEX D

List of Substances Subject to Authorisation

Name	Description	EC no.	CAS no.	Entry no.	Sunset Date	Latest application date	Intrinsic property(ies) referred to in Article 57	Exempted (categories of) uses
1,2-dichloroethane (EDC)		203-458-1	107-06-2	26	22/11/2017	22/05/2016	Carcinogenic (Article 57a)	
2,2'-dichloro-4,4'-methylene dianiline (MOCA)		202-918-9	101-14-4	27	22/11/2017	22/05/2016	Carcinogenic (Article 57a)	
2,4-dinitrotoluene (2,4-DNT)		204-450-0	121-14-2	14	21/08/2015	21/02/2014	Carcinogenic (Article 57a)	
4,4’-Diaminodiphenylmethane (MDA)		202-974-4	101-77-9	2	21/08/2014	21/02/2013	Carcinogenic (Article 57a)	
5-tert-butyl-2,4,6-trinitro-m-xylene (Musk xylene)		201-329-4	81-15-2	1	21/08/2014	21/02/2013	vPvB (Article 57 e)	
Acids generated from chromium trioxide and their oligomers		-	-	17	21/09/2017	21/03/2016	Carcinogenic (Article 57a)	
Oligomers of chromic acid and dichromic acid		-	-	17	21/09/2017	21/03/2016	Carcinogenic (Article 57a)	
Dichromic acid		236-881-5	13530-68-2	17	21/09/2017	21/03/2016	Carcinogenic (Article 57a)	
Chromic acid		231-801-5	7738-94-5	17	21/09/2017	21/03/2016	Carcinogenic (Article 57a)	
Ammonium dichromate		232-143-1	7789-09-5	20	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)#Toxic for reproduction (Article 57c)	
Arsenic acid		231-901-9	7778-39-4	24	22/08/2017	22/02/2016	Carcinogenic (Article 57a)	
Benzyl butyl phthalate (BBP)		201-622-7	85-68-7	5	21/02/2015	21/08/2013	Toxic for reproduction (Article 57c)	Uses in the immediate packaging of medicinal products covered under Regulation (EC) No 726/2004, Directive 2 001/82/EC, and/or Directive

								2001/83/EC.
Bis(2-ethylhexyl) phthalate (DEHP)		204-211-0	117-81-7	4	21/02/2015	21/08/2013	Toxic for reproduction (Article 57c)	Uses in the immediate packaging of medicinal products covered under Regulation (EC) No 726/2004, Directive 2001/82/EC, and/or Directive 2001/83/EC.
Bis(2-methoxyethyl) ether		203-924-4	111-96-6	25	22/08/2017	22/02/2016	Toxic for reproduction (Article 57c)	
Chromium trioxide		215-607-8	1333-82-0	16	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)	
Diarsenic pentaoxide		215-116-9	1303-28-2	9	21/05/2015	21/11/2013	Carcinogenic (Article 57a)	
Diarsenic trioxide		215-481-4	1327-53-3	8	21/05/2015	21/11/2013	Carcinogenic (Article 57a)	
Dibutyl phthalate (DBP)		201-557-4	84-74-2	6	21/02/2015	21/08/2013	Toxic for reproduction (Article 57c)	Uses in the immediate packaging of medicinal products covered under Regulation (EC) No 726/2004, Directive 2 001/82/EC, and/or Directive 2001/83/EC.
Dichromium tris(chromate)		246-356-2	24613-89-6	28	22/01/2019	22/07/2017	Carcinogenic (Article 57a)	
Diisobutyl phthalate (DIBP)		201-553-2	84-69-5	7	21/02/2015	21/08/2013	Toxic for reproduction (Article 57c)	
Formaldehyde, oligomeric reaction products with aniline		500-036-1	25214-70-4	23	22/08/2017	22/02/2016	Carcinogenic (Article 57a)	
Hexabromocyclododecane (HBCDD)	and all major diastereoisomers identified	-	-	3	21/08/2015	21/02/2014	PBT (Article 57 d)	
gamma-hexabromocyclododec		-	134237-52-8	3	21/08/2015	21/02/2014	PBT (Article 57 d)	

ane								
beta-hexabromocyclododecane		-	134237-51-7	3	21/08/2015	21/02/2014	PBT (Article 57 d)	
Hexabromocyclododecane		247-148-4	25637-99-4	3	21/08/2015	21/02/2014	PBT (Article 57 d)	
1,2,5,6,9,10-hexabromocyclodecane		221-695-9	3194-55-6	3	21/08/2015	21/02/2014	PBT (Article 57 d)	
alpha-hexabromocyclododecane		-	134237-50-6	3	21/08/2015	21/02/2014	PBT (Article 57 d)	
Lead chromate		231-846-0	7758-97-6	10	21/05/2015	21/11/2013	Carcinogenic (Article 57a)#Toxic for reproduction (Article 57c)	
Lead chromate molybdate sulfate red	-	235-759-9	12656-85-8	12	21/05/2015	21/11/2013	Carcinogenic (Article 57a)#Toxic for reproduction (Article 57c)	
Lead sulfochromate yellow	-	215-693-7	1344-37-2	11	21/05/2015	21/11/2013	Carcinogenic (Article 57a)#Toxic for reproduction (Article 57c)	
Pentazinc chromate octahydroxide		256-418-0	49663-84-5	31	22/01/2019	22/07/2017	Carcinogenic (Article 57a)	
Potassium chromate		232-140-5	7789-00-6	21	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)	
Potassium dichromate		231-906-6	7778-50-9	19	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)#Toxic for reproduction (Article 57c)	
Potassium hydroxyoctaoxodizincatedichromate		234-329-8	11103-86-9	30	22/01/2019	22/07/2017	Carcinogenic (Article 57a)	
Sodium chromate		231-889-5	7775-11-3	22	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)#Toxic for reproduction (Article 57c)	
Sodium dichromate		234-190-3	10588-01-9, 7789-12-0	18	21/09/2017	21/03/2016	Carcinogenic (Article 57a)#Mutagenic (Article 57b)#Toxic for reproduction (Article 57c)	
Strontium chromate		232-142-6	7789-06-2	29	22/01/2019	22/07/2017	Carcinogenic (Article 57a)	
Trichloroethylene		201-167-4	79-01-6	15	21/04/2016	21/10/2014	Carcinogenic (Article 57a)	
Tris(2-chloroethyl) phosphate		204-118-5	115-96-8	13	21/08/2015	21/02/2014	Toxic for reproduction (Article 57c)	

(**for more information:**https://echa.europa.eu/addressing-chemicals-of-concern/authorisation/recommendation-for-inclusion-in-the-authorisation-list/authorisation-list)

ANNEX E

THE PROJECT TEAM

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Name Surname	: Gazanfer ERBAY
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EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Ph.D	Geology Engineering	Suleyman Demirel University	1998
Master	Geology Engineering	Suleyman Demirel University	1993
Undergraduate	Geology Engineering	Hacettepe University	1989

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2009-Present	Karabuk Provincial Disaster and Emergency Directorate	Manrager
2001-2009	Ministry Of Public Works And Settlement	Manager
1990-2001	Mineral Research & Exploration General Directorate	Engineer

PERSONAL INFORMATION

Name Surname	: Fatma Serap GÜLEÇ
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EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Master	Energy Systems Engineering	Karabuk University	2015
Undergraduate	Chemical Engineering	Hacettepe University	2007

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2007	KARDEMIR Iron &Steel Company	Water Facilities Chief Engineer

PERSONAL INFORMATION

Name Surname	: Ilhan ATTAR
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EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Undergraduate	Chemical Engineering	Middle East Technical University	1999

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2014	KARDEMIR Iron &Steel Company	Ch. Engineer
2010	SOCAR&Turcas PETKIM Petrochemical Industry	Project Engineer
2001	ERDEMIR Iron &Steel Company	Ch. Engineer
2001	Ankara Criminal Laboratory	Ch. Engineer

PERSONAL INFORMATION

Name Surname	: Muge CEBECİ
Date of birth and place	: 1981, Karabuk, Turkey
Foreign Languages	:English
E-mail	:mcebeci@kardemir.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Master	Energy Systems Engineering	Karabuk University	2013
Undergraduate	Environmental Engineering	19 May University	2004

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2004	KADIOĞLU Mining Company	Quality Engineer
2004	CEBECİ Environmental Consulting	Environmental Engineering
2006	KARDEMIR Iron &Steel Company	Environmental Management Chief Engineer

PERSONAL INFORMATION

Name Surname	: Nuretttin ELTUGRAL
Date of birth and place	:1980,
Foreign Languages	:English, Italian
E-mail	:nurettineltugral@karabuk.edu.tr

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Ph.D	Department of Chemistry and Industrial Chemistry	Pisa University	2010
Master	Department of Chemistry	Bogazici University	2006
Undergraduate	Department of Chemistry	İzmir Institute of Technology	2003

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2011-present	Karabuk University/ Metallurgical and Materials Engineering Department	Assistant Professor

PERSONAL INFORMATION

Name Surname	: Yasin KANBUR
Date of birth and place	: 24.10.1979 – Bremen (D)
Foreign Languages	: English
E-mail	:yasinkanbur@karabuk.edu.tr

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Ph.D	Polymer Science and Technology	Middle East Technical University	2011
Master	----	----	----
Undergraduate	Chemistry	Middle East Technical University	2002

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2002-2003	Ministry of National Education / Turkey	Teacher
2004-2011	Middle East Technical University	Research Assistant
2011-2012	Atatürk University	Research Assistant
2012-Continue	Karabük University	Assist.Prof.Dr
2014-2015	Johannes Keppler University / Linz Institute for Organic Solar Cells	Post Doctoral Assistant
2015-Continue	Karabük University Iron and Steel Institute	Vice Director

PERSONAL INFORMATION

Name Surname	: Kalle Heikki RAJANTIE
Date of birth and place	:1958, Ilomantsi, Finland
Foreign Languages	:Finnish, Swedish, Germany, English, Portuguese
E-mail	:kalle.rajantie@hamk.fi

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Ph. D (1st doctoral degree, Lic.Techn.)	Civil engineering	Helsinki University of Technology	1991
Master	Civil Engineering	Helsinki University of Technology	1985
Undergraduate	Vocational education	HAMK UAS	2000

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
1998- present	HAMK university of applied sciences	Principal lecturer
1991-1998	AEL Ltd	Manager
1987-1991	Finnish Ministry of Foreign Affairs and Plancenter Ltd	Water expert in Mozambique
1983-1987	Helsinki university of technology	Research worker

PERSONAL INFORMATION

Name Surname	Sakari HALMEMIES
Date of birth and place	1952, Jyväskylä, Finland
Foreign Languages	English, Swedish
E-mail	sakari.halmemies@lamk.fi

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
DSc (Tech)	Environmental Technology	Tampere University of Technology	2003
MSc	Chemistry, Chemical Engineering	Helsinki University of Technology	1977
Undergraduate	Pedagogical Competence	Jyväskylä University of Applied Sciences	1999

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2004- present job	Lahti University of Applied Sciences	Principal Lecturer on Environmental Technology
1992-2004	Emergency Services College	Head Instructor on Hazardous Materials
1983-1992	Valio Engineering, Alfa-Laval, Ekono Engineering	Project Engineer on Food Industrial processes

PERSONAL INFORMATION

Name Surname	: Bora BALUN
Date of birth and place	:1977, Adana, Turkey
Foreign Languages	:English
E-mail	:borabalun@hotmail.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Ph.D	Labor Economics and Industrial Relations	Anadolu University	2016-Present
Master	International Relations	Selcuk University	2012
Undergraduate	Labor Economics and Industrial Relations	Anadolu University	2009

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2012-present	Karabuk Provincial Disaster and Emergency Directorate	Branch Manager
1995-2012	Turkish Armed Forces, Gendarmerie General Command	Team Personnel

PERSONAL INFORMATION

Name Surname	: ANA ROCHA
Date of birth and place	:1985, Ponte de Lima, Portugal
Foreign Languages	:English
E-mail	:anacristinafrocha@gmail.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Master	Integrated management systems - quality, environment and safety	IPCA-Barcelos	2012
Undergraduate	Environmental health	ESTeS Coimbra	2007

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2008-present	Previform, Laboratório, Formação, Higiene Segurança no Trabalho, Lda	Technician's of Hygiene and Safety at Work, Auditor and consultant in the area of hygiene and food safety and training

PERSONAL INFORMATION

Name Surname	: Marta COELHO
Date of birth and place	:1976, Arcos de Valdevez, Portugal
Foreign Languages	: English
E-mail	:marta.maria.coelho@gmail.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Master	Occupational safety	GTI – Gestão, Tecnologia e Inovação	2005
Undergraduate	Geography and Planning	Minho University	2001

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2006-present	Previform, Laboratório, Formação, Higiene Segurança no Trabalho, Lda	Services of Hygiene and Safety at Work, training and laboratory
2005-2006	Municipality of Arcos de Valdevez	Technician of planning and urbanism

PERSONAL INFORMATION

Name Surname	: Iñigo Marañón Romero
Date of birth and place	: 1980, Pamplona, Spain
Foreign Languages	: English
E-mail	: imaranon@tesicnor.com

EDUCATION

Degree	**Department**	**University**	**Date of Graduation**
Certification	Security Director Ministry of Home	Security Director Ministry of Home	Security Director Ministry of Home
Certification	Dangerous Goods Safety	Dangerous Goods Safety	Dangerous Goods Safety
Master	Labour Risk Prevention	Labour Risk Prevention	Labour Risk Prevention
Undergraduate	Chemical Engineer University of King	Chemical Engineer University of King	Chemical Engineer University of King

WORK EXPERIENCE

Year	**Corporation/Institute**	**Occupation or position**
2016-Present	Tesicnor S.L. Manager of the Industrial Safety	Tesicnor S.L. Manager of the Industrial Safety
2004-2006	MGO Group Industrial Safety Engineer	MGO Group Industrial Safety Engineer

ANNEX F

THE PROJECT MEETINGS

Portugal Meeting

Finland Meeting

Kickoff meeting (Turkey)

Spain Meeting

The Final Meeting (Turkey)

QUESTİONNAIRE PRACTICES

KARDEMIR CO.

Karabuk University

HAMK University

ACTIVITIES

TRAINING MODULES ON CHEMICAL SAFETY

Omnipresent Project 2015-2017

Accident Prevention, Preparedness and Response

SEVESO

A new Directive on the control of major accident hazards involving dangerous substances

REACH

COMPLIANCE

Registration, Evaluation, Authorisation and Restriction of Chemicals

KARDEMIR's steel factory is one of the end users of project results.

Background

The effects of industrial accidents do not stop at national borders. EU and Turkish citizens can be seriously affected by accidents in neighbouring countries. Therefore it is necessary to co-operate internationally and to aim at a high level of protection also in non-EU countries.

Response

A typical transportation accident of a gasoline tanker

A typical leakage of toxic NOx gases

Aim of the project

to increase partner countries' understanding of issues related to chemical accident prevention and preparedness

to improve the capacity of relevant institutions, agencies and experts to address the risks of chemical accidents

to help countries to develop and implement an appropriate chemical accident prevention and preparedness guidebook

Themes for training modules

Risk Analysis, Risk Assessment, Risk, Management, Response, Safety Rules, Regulations, Chemical Accidents, Health, Environmental, Classification, Precautions, Implementation

Training Program

Partners

Turkey	Karabuk Provincial Disaster and Emergency Management Turkey, Karabuk University and Kardemir Karabuk Iron steel Industry and Trade Company
Spain	Safety consulting company TESICNOR S.L.
Portugal	Vocational Training, Safety and Health Work, Food Safety, and environmental management called PREVIFORM
Finland	Lahti University of Applied Sciences Häme University of Applied Sciences

Outputs of the project

Competency Based Education Modules for safety professionals
Guidebook for prevention, preparedness and response of chemical accidents
Web pages on the results of the project

Co-funded by the Erasmus+ Programme of the European Union

Activities in Finland

← TESICNOR SEGURIDAD INDUSTRIAL SE FORMA EN SUESKOLA

CONSULTA CONSEJERO DE SEGURIDAD: RECEPCIÓN DE GASOIL EN PEQUEÑAS CANTIDADES, MODOS DE EFECTUAR EL TRANSPORTE Y OBLIGACIONES →

TESICNOR COLABORA EN EL PROYECTO EUROPEO "OMNIPRESENT PROJECT"

Publicado el Marzo 1, 2016 por Rubén Hernández Librán

Desde el pasado 18 de febrero hasta el 21, **Tesicnor Seguridad Industrial** y **Tesicnor Formación** estuvieron presentes en la reunión de inicio celebrada en Turquía del proyecto "***FORMING THE COMPETENCY BASED EDUCATION MODULES FOR CHEMICAL ACCIDENT PREVENTION, PREPAREDNESS AND RESPONSE***" (Omnipresent Project).

Aquí podéis ver el programa del mismo desde la página de European Commission.

Subscríbete a TEN SAFETY TWEETS

Para suscribirte déjanos tus datos. Te mandaremos un correo de confirmación.

Categorías

- ANÁLISIS DE RIESGOS
- ATEX
- AUTOPROTECCIÓN
- CONSEJERO
- LOTO
- RIESGO MEDIOAMBIENTAL
- SEVESO
- TESICNOR
- Varios

Activities in Spain

WORKSHOP in TURKEY


Forming the Competen
Accident Preven
«STOR
THE FINAL MEETING
25-27 September 2017, Karabuk, TURKEY
25-27 Eylül 2017, Karabük, TÜRKİYE
HAMK
PREV/FORM
26.09.2017


Transportation
HAMK
PREV/FORM
26.09.2017


Forming The Compet
Based Education Mod
For Chemical Accid
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And Response
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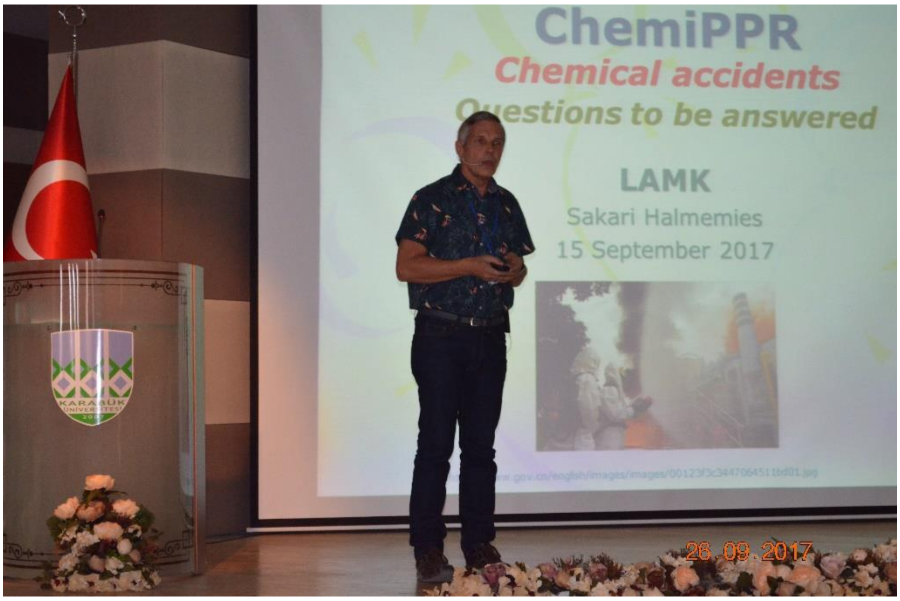
PREV/FORM
26.09.2017



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