Final report Annex 1: Elements to be considered in the initial screening (Task 1)

Development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances (070307/2013/655473/ENV.C3)

Report for the European Commission (DG Environment)

AMEC Environment & Infrastructure UK Limited

In association with INERIS and EU-VRi

December 2014

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European Commission (DG Environment)

Development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances

Final report – Annex 1

AMEC Environment & Infrastructure
UK Limited

December 2014

List of Abbreviations

ADAM	Accident Damage Assessment Module
ADR	European Agreement Concerning The International Carriage Of Dangerous Goods By Road
ALARP	As Low As Reasonably Practicable
ARIA	Analysis, Research and Information about Accidents
BLEVE	Boiling Liquid Expanding Vapour Explosion
BOD – COD	Biochemical Oxygen Demand – Chemical Oxygen Demand
CE	Critical Event
CFD	Computational Fluid Dynamics
CLP	Classification Labelling Packaging
COMAH	Control Of Major Accident Hazards
DA	Deterministic Approach
ECHA	European Chemicals Agency
e-MARS	Major Accident Reporting System
EU	European Union
EWGLUP	European Working Group on Land Use Planning
F&EI	Fire & Explosion Index
GHS	Globally Harmonised System
JRC	Joint Research Centre
LPG	Liquefied Petroleum Gas
LUP	Land-Use Planning
MAHB	Major Accident Hazard Bureau
MATTE	Major Accident To The Environment
M_F	Material Factor of the Dow’s Fire & Explosion Index
MIMAH	Methodology for Identification of Major Accident Hazards
NFPA	National Fire Protection Agency
NOEC	No Observable Adverse Effects Concentration
PA	Probabilistic Approach
PLG	Pressurised Liquefied Gas

RID	European Agreement Concerning the International Carriage of Dangerous Goods by Rail
RMP	Risk Management Plan
STOT-SE	Specific Target Organ Toxicity (Single Exposure)
USEPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion

Physicochemical parameters

BCF	Bioconcentration Factor
EC_{50}	Median Effective Concentration
ΔH_r	Standard enthalpy of reaction
K_{st} / K_g	Maximum rate of explosion pressure rise for dust clouds/gas
LD_{50} / LC_{50}	Median Lethal Dose / Median Lethal Concentration
LFL / LEL	Lower Flammability Limit / Lower Explosion Limit
LOC	Limiting Oxygen Concentration
MIE	Minimum Ignition Energy
MTSR	Maximum Temperature of the Reaction Synthesis
NOEC	No Observed Effect Concentration
P_{max}	Maximum explosion pressure
P_{vap}	Vapour pressure
ΔT_{ad}	Adiabatic temperature rise
T_{eb}	Boiling point
TMR_{ad}	Time to maximum rate in adiabatic condition
UFL / UEL	Upper Flammability Limit / Upper Explosion Limit

Contents

Introduction

Purpose of this report

This report forms part of the outputs of a contract for the European Commission on ‘development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances’. The work has been undertaken by AMEC, INERIS and EU-VRi.

The present report concerns one of a number of specific tasks under the project. It should not be read in isolation, but in conjunction with the main report and in conjunction with the reports concerning the other project tasks.

Scope of Task 1

Article 4 of the Seveso III Directive introduces, in its first paragraph, three criteria that should be taken into account when an exclusion from the scope of Seveso III is considered:

- The physical form of the dangerous substance under normal processing or handling conditions or in an unplanned loss of containment[1];
- The inherent properties of the dangerous substance, in particular those related to dispersive behaviour in a major-accident scenario, such as molecular mass and saturated vapour pressure;
- The maximum concentration of the substance in the case of mixtures.

The same article also introduces, in its third paragraph, a list of information related to the substance to be provided in the request for exclusion:

- A comprehensive list of properties necessary to assess the dangerous substance’s potential for causing physical, health or environmental harm;
- Physical and chemical properties (for instance molecular mass, saturated vapour pressure, inherent toxicity, boiling point, reactivity, viscosity, solubility and other relevant properties);
- Health and physical properties (for instance reactivity, flammability, toxicity together with additional factors such as mode of attack on the body, injury to fatality ratio and long term effects and other properties as relevant);

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[1] The containment and generic packing of the dangerous substance should, where appropriate, also be taken into account, including in particular where covered under specific Union legislation.

- Environmental hazard properties (for instance ecotoxicity, persistence, bio-accumulation, potential for long-range environmental transport, and other properties as relevant);
- Where available, the Union classification of the substance or mixture;
- Information about substance-specific operating conditions under which the dangerous substance is stored, used and/or may be present in the event of foreseeable abnormal operations or an accident such as fire.

Thus, Article 4 focuses on the dangerous substances, their nature, their properties, their conditions of use and the associated risks. In an industrial context, the risk is always related to the storage, the use, the transformation and/or the transport of dangerous chemical substances and/ or mixtures. In an early stage of any risk assessment, it is therefore essential to have a very good knowledge of the chemicals handled on the industrial site. In the context of risk assessment, this means being able to identify the hazards associated with a chemical and then being able to anticipate the accidental risks that can be caused by the use of this substance.

This task aims to further specify the characteristics mentioned in Article 4(1)(a) to (c) and the information referred to in Article 4(3)(a) to (f) that need to be provided by the Member State in order to be of use during the envisaged "initial screening" stage. At this first stage of the process, the principal objective is to provide explanations on how to make use of information regarding the physical, chemical, health hazard, physical hazard and environment hazard properties of a substance as well as of its operating conditions.

The initial screening is not expected to be sufficient to conclude as to the impossibility for a substance to create a major accident. Its main purpose would be to enable identification of cases for which this impossibility clearly does not exist.

Scope of exclusions under Article 4

Article 4 of the Seveso III Directive provides for exemption of substances from the entire scope of the directive. This means that a proposal for exemption has to be justified on the basis that major accidents can be ruled out across the EU, taking into account both current use of a substance and reasonably foreseeable future uses.

It is relevant to note that dispensations (limitations) on the information to be included in safety reports (for high tier establishments) were possible under Article 9(6) of the Seveso II Directive. Indeed, the criteria developed for dispensations under Article 9(6)[2] have some overlaps with those adopted in the context of Article 4 of Seveso III, though in practice the way in which they can be used is markedly different (establishment-level dispensation under Seveso II Article 9(6) versus EU level exclusion from scope under Seveso III Article 4).

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[2] Physical form; containment and quantities; location and quantities; and classification. This is set out in Commission Decision 98/433/EC of 8 July 1998. Further details are provided in: 'Explanations and guidelines for the application of the dispensation rule of article 9, paragraph 6 of Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances, European Commission Joint Research Centre, 1998.

Appendix A to the present document provides a summary of the dispensations possible under Article 4 of Seveso III and Article 9(6) of Seveso II. It also includes a review of the criteria for dispensation under Article 9(6), examples of the dispensations that have been applied, and the relevance of the dispensation criteria to the Article 4 assessment methodology. It is important to note that relatively few dispensations have been granted under Seveso II Article 9(6) and that the majority of dispensations under Seveso II related to the site-specific conditions in which a substance was held/used (for example related to containment, quantity and location of storage at a particular site, or the fact that a substance is not pressurised at a particular site). There was however one example of a substance excluded in relation to its physical form in general terms.

Unlike Seveso III Article 4, the dispensations under Seveso II Article 9(6) only required notification to the Commission. There was no requirement for assessment of the dispensations for consistency with the established criteria, nor for approval of the dispensations.

While the dispensations under Article 9(6) of Seveso II provide useful insights into potential exclusions from scope under Article 4 of Seveso III, it is also clear that the typical basis for those dispensations is unlikely to apply at EU level in many cases. There are few EU-wide rules on for example containment and packaging that would eliminate the potential for a major accident and hence justify an EU-wide exclusion from the scope of Seveso.

Overall, therefore, the level of effort required in justifying an exemption is expected to be substantially greater under Article 4 than under Article 9(6) of Seveso II, due to the need to exclude major accidents from all existing and possible future establishments across the EU.

Structure of this report

To provide a basic guideline that is as practical as possible for the reader, this report has been divided into two main parts:

- The first part gives general explanations about the main physicochemical properties of a substance and highlights their link with the dangerous phenomena that may be generated in case of an accident. The objective of this part is to describe in a detailed manner the elements which Member States should consider in the initial screening stage to check whether a certain substance could cause a release of matter or energy that could create a major accident.

  The first part is divided as follows:

  - Presentation of the different hazards of chemical substances;
  - Overview of the different dangerous phenomena that can occur in an industrial context and their possible effects;
  - List of parameters which are generally used in a risk identification process and link with the dangerous phenomena.

- The second part refers to the stages of the initial screening itself. Guidance is given regarding the concrete steps that could be undertaken by member states as part of the initial screening. The objective is to ensure that the member state covers each of the key physicochemical properties of the substance under assessment and draws conclusions on the ability to cause dangerous phenomena in relation to those properties.

Part 1

Physicochemical properties and link with dangerous phenomena

1. General Considerations

1.1 Review of the main chemical and physical properties for substances

1.1.1 Basic substance properties

When considering a chemical substance on an industrial site (or on sites in general), the first thing to do is to collect some basic information: the correct chemical name of the substance (sometimes only the commercial name is provided), its structural chemical formula (important to observe the structure of the molecule) and its physical form in the context of its use.

Different forms of a substance may result in different hazards. The three physical forms of matter very well-known and observable in everyday life are: solid, liquid and gas[3] (cf. Figure 1.1). Other relevant forms include powder, dust and mist. Mist refers to liquid droplets of a substance or mixture suspended in air or another gas.

Depending on the condition of a process, a chemical can exist under multiple forms on any one industrial site: for example a liquid solvent which is heated in a reactor can boil and then generate vapour (e.g. a solvent such as benzene boils at 80°C); a solid which is heated can melt and become liquid (a salt such as potassium nitrate melts at 334°C). The changes of physical form that can typically occur include: melting, freezing, sublimation, deposition, vaporisation and condensation (cf. Figure 1.1). For each change of physical form of each component the temperature has a specific name:

- The melting point or melting temperature of a solid is the temperature at which it changes form from solid to liquid at a specified pressure (normally taken to be atmospheric unless stated otherwise). At the melting point, the solid and liquid phases exist in equilibrium[4]. The melting point of a substance depends (usually slightly) on pressure and is usually specified at standard pressure (101.3 kPa = 1 bar). When considered as the temperature of the reverse change from liquid to solid, it is referred to as the freezing point or crystallisation point.
- The boiling point or boiling temperature of a liquid is the temperature at which it changes form from liquid to vapour at atmosphere pressure. At the boiling point, the liquid and vapour phases exist in equilibrium. The boiling point depends on pressure and is usually specified at standard pressure. When considered as the temperature of the reverse change from vapour to liquid, it is referred to as the condensation point.

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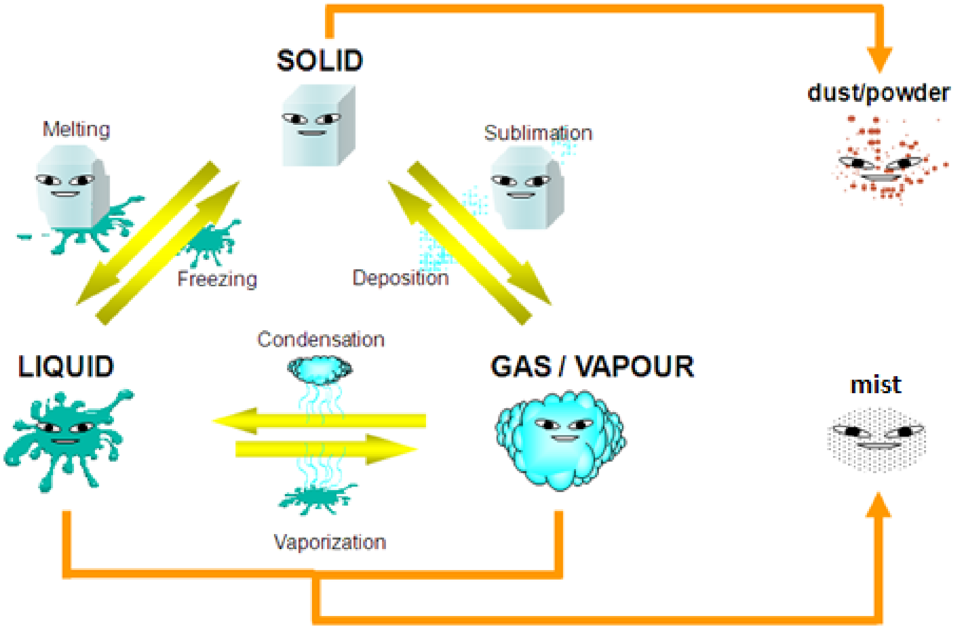
[3] Definitions are provided in Annex I Part 1 of the CLP regulation [Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing. Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006].

[4] CRC, Handbook of Chemistry and Physics, David R.Lide, 85th Edition, 2004-2005.

Figure 1.1 Different possible physical forms of a chemical substance



As already noted, it is important to consider the form of the substance while searching for the associated risks. For instance, the potential for a dust explosion will also depend on the size of the particles. The size of the particles must be small enough to form an explosive atmosphere (generally under 500 microns).

1.1.2 Substance purity

The second thing to check is the purity of the substance: is the substance pure or used in a mixture? If the substance is a mixture, it is important to list the different components of the mixture and the concentration of each component. For instance, aqueous solution of nitric acid can be bought in concentrations going from less than 10% to 99.999%.

It is important to underline that even when a substance is qualified as pure, trace impurities are present. It is possible to increase the level of impurities to make the substance less harmful. For example, for thermally unstable substances which tend to polymerise (e.g. acrylic acid or methacrylic acid), some small amounts (parts per million) of polymerisation inhibitors may be added to decrease the risk of reaction.

In term of vocabulary and according to CLP, the word ‘substance’ will refer to 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 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”. The word ‘mixture’ will refer to a “mixture or solution composed of two or more substances”.

In general, when considering a dangerous substance in a solution, the higher the concentration of the substance the higher the risk. A nitric acid solution at 99.999% would be more corrosive than a nitric acid solution at 10%. Likewise, diluting a dangerous substance or mixing it with less dangerous substance may decrease the hazard.

Thus, 1% of a thermally unstable substance in 99% of water would virtually eliminate the risk of explosion. When working with mixtures, it can be useful to pay attention to the solubility of the substances:

- The solubility is a quantity expressing the maximum concentration of some material (the solute) that can exist in another liquid or solid material (the solvent) at thermodynamic equilibrium at specified temperature and pressure. Common measures of solubility include the mass of solute per unit mass of solution (mass fraction) but also mole fraction of solute[5].

1.1.3 Substance characterisation

Once the above information has been collected, some intrinsic properties can be used to characterise the substance, including: the molar mass, the mass density, the viscosity, the surface tension and the vapour pressure[36].

- The molar mass is the mass of one mole of substance. It is normally expressed in units of g/mol and noted M. For instance, the molar mass of Carbon (C) is 12 g/mol.

- The mass density is the mass of a sample or body divided by the volume. It is typically expressed in units of kg/m3. For instance, the density of water is 1,000 kg/m3. In the case of a gas release in a room, a gas which is more dense than air will tend to go towards the ground, whereas a lighter gas than air will tend to go to the roof.

- The viscosity (for a liquid) of a substance is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal notion of "thickness". Water has a viscosity of 1 centipoise (or 1 cP = 1 mPa.s) at 20°C. Glycerine has a higher viscosity than water.

- The granulometry (for solid dust/powder) is the measurement of particle size distribution in a collection of grains. This is an important parameter for dust explosions: if the size of the particles is too big (for example more than 500 micron) the dust will not explode.

- The surface tension (for a liquid), generally noted γ or σ, is the force per unit length in the plane of the interface between a liquid and a gas, which resists an increase in the area of the surface. It is a contractive tendency of the surface of a liquid that allows it to resist an external force. Water has a high surface tension equal to 72.75 mN/m at 20°C.

- The vapour pressure (for a liquid) is also an important parameter. An example can be given for hydrochloric acid: At 20°C, the vapour pressure of hydrochloric acid concentrated at 33% is 5.1 kPa and it is 2.2 kPa for hydrochloric acid concentrated at 30%. Toxic effects will be higher for hydrochloric acid concentrated at 33% because of the greater tendency to escape from the liquid into the air.

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[5] CRC, Handbook of Chemistry and Physics, David R.Lide, 85th Edition, 2004-2005

[6] Lees' Loss Prevention in the Process Industries, table 8.5, p. 214

1.2 Substance-specific operating conditions

It is also very important to check how the substance is used, where it is used and under which conditions. It is important for two principal reasons:

- Most of the physicochemical properties of a substance depend on the conditions of pressure and temperature. For instance, boiling temperature would depend on the pressure; viscosity would depend on the temperature; the physical form of a substance would depend on the temperature and pressure.
- **The hazard of a substance is intrinsic to the substance, but the risks are always related to the environment or the conditions of use.** For instance, a flammable liquid used at a temperature much below its flash point has no risk of ignition: the hazard is still there but there is no risk of the temperature exceeding the flash point.

The following is a (non-exhaustive) list of questions that it can be relevant to ask regarding the conditions of use in the context of operating conditions that can affect the potential for an accident:

- Is the substance stored? Is the substance used as a reactant? Is the substance an intermediate? Is the substance used as a catalyst? Is the substance used as a cooling fluid? Is the substance transformed during a reaction?
- Is the substance stored in a dedicated building? In what container is the substance stored? Does it flow in pipes? Is it carried out in a reactor? For instance, iron can catalyse the decomposition of peroxide, it is then important to check the composition material of the container in which the peroxide is transported to check any incompatibility.
- Under what conditions, essentially temperature, pressure and volume (or flow rate), is the substance used?

The nature of the storage can have an influence on the substance’s behaviour: in some cases, chemical interactions can occur between the substance and the container, for instance iron can catalyse the decomposition of certain peroxides; chemical incompatibilities between a corrosive liquid and a metallic container can lead to a leak.

Thus specific-operating conditions in the event of foreseeable abnormal operations, as well as the packaging/containment, are important to consider. The link between these conditions and the potential accident scenarios is discussed in Tasks 4 and 5.

1.3 Key points

As a conclusion of this first step, before any further study, it is important to have basic information when dealing with a substance:

- Its correct names (commercial, chemical) and its formula.
- Some basic characteristics such as molar mass and mass density.
- The physical form of the substance.

- The concentration of the substance if used in a mixture.
- The conditions of use of the substance.

2. Hazards of Chemicals: General Overview

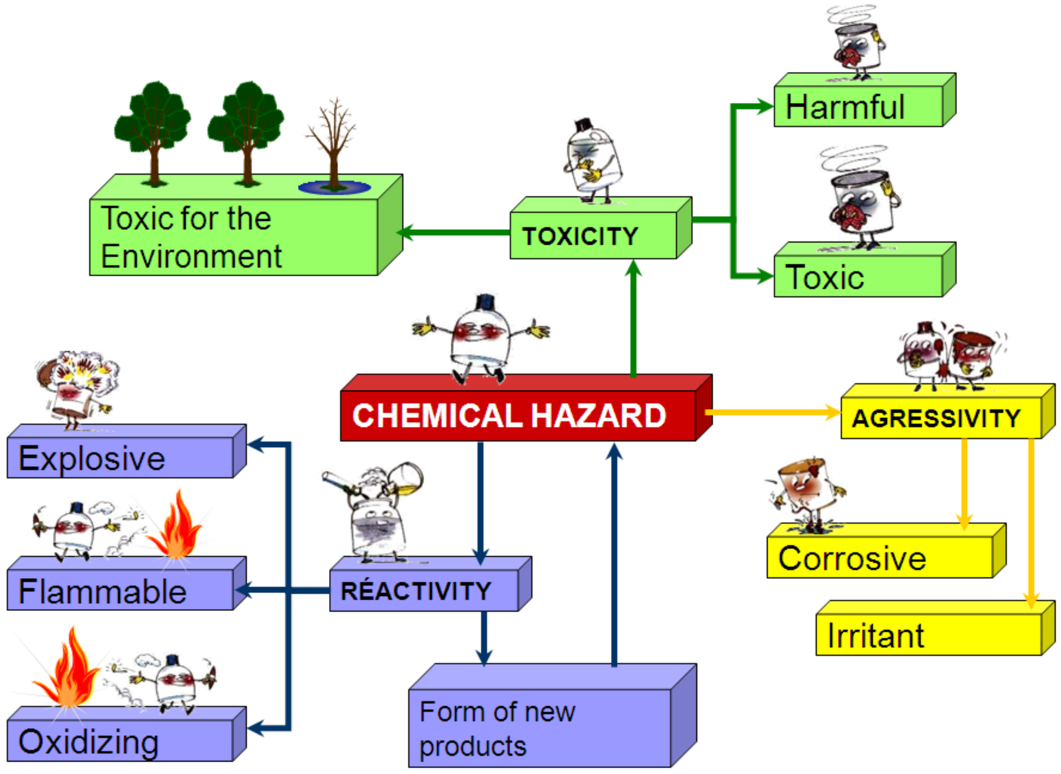
The term ‘hazard’ refers to a potential source of harm. This notion defines an intrinsic property of a substance that can cause harm or damage to a vulnerable element (humans, property or the environment).

For instance:

- Phosgene is toxic;
- Ethylene is flammable;
- Benzyl peroxide is explosive;
- Vapour under a pressure of 4,000 kPa in a closed container represents an important source of energy.

Figure 2.1 summarises in a simple graphic the different types of hazards for chemicals.

Figure 2.1 Typology of hazards related to chemical substances



A more complete list of hazards is available in the CLP regulation[7]. The aim of this regulation is to classify and label by identifying the hazardous properties of a substance or a mixture. According to the CLP regulation, the hazards are divided into three main categories: physical, health and environmental. These three categories are divided into several hazard classes: 16 classes of physical hazards, 10 classes of health hazards and 2 classes of environmental hazards (cf. Table 2.1).

Table 2.1 Hazard classification according to CLP

	Physical Hazards	**Health Hazards**	**Environmental Hazards**
1	Explosive	Acute toxicity	Hazardous to the aquatic environment
2	Flammable gas	Skin corrosion/irritation	Hazardous to the ozone layer
3	Flammable aerosols	Serious eye damage/eye irritation	
4	Oxidizing gas	Skin sensitisation	
5	Gas under pressure	Germ cell mutagenicity	
6	Flammable liquid	Carcinogenicity	
7	Flammable solid	Reproductive toxicity	
8	Self-reactive substance	Specific target organ toxicity – Single exposure (STOT – SE)	
9	Pyrophoric liquid	Specific target organ toxicity – Repeated exposure (STOT – RE)	
10	Pyrophoric solid	Respiratory sensitisation	
11	Self-heating substance and mixture		
12	Substance and mixture which, in contact of water, emit flammable gas		
13	Oxidising liquid		
14	Oxidising solids		
15	Organic peroxide		
16	Corrosive to metal		

Annex VI to Regulation (EC) No 1272/2008 includes a list of harmonised classification and labelling for more than 4,000 substances or groups of substances (representing about one third of the substances registered in the ECHA database[8]) which are legally binding within the European Union. For instance, hydrogen (H_2) which is a gas at

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[7] See http://echa.europa.eu/fr/addressing-chemicals-of-concern/harmonised-classification-and-labelling/annex-vi-to-clp

[8] ECHA (European Chemicals Agency) Database: http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances

ambient temperature and atmospheric pressure is classified as a flammable gas and gas under pressure. The classification depends on the properties of the substances and mixtures. If a substance or mixture is not included in Annex VI, the regulation defines tests that can be used to decide if the substance has to be classified and, if so, in which categories. These tests are defined in the Manual of Tests and Criteria of the UN Recommendation on the Transport of Dangerous Goods[9]. It is important to note that a substance may pertain to more than one hazard category and that the harmonised classification only applies for a certain category. For the other categories, self-classification may need to be applied. For mixtures, there is no harmonised classification.

In the context of risk assessment, the 16 physical hazards can play a role in the definition of major accident scenarios. Concerning health hazards, only the "acute toxicity" and the "specific target organ toxicity – Single exposure (STOT –SE)" have to be considered. The environmental hazards relevant in the context of the assessment methodology are the hazards to the aquatic environment. For each of these hazards, a brief overview of the properties concerned is given in Section 4. The ECHA website provides relevant information, in particular in the document "Guidance on the Application of the CLP Criteria"[10].

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[9] http://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev5/English/ST-SG-AC10-11-Rev5-EN.pdf

[10] http://echa.europa.eu/documents/10162/13562/clp_en.pdf

3. Dangerous Phenomena and their Effects

3.1 Background

As seen in the previous section, the notion of “hazard” defines an intrinsic property of the substance. The use of a hazardous substance can lead to the development of dangerous phenomena.

Dangerous phenomena occurring in the industry are generally classified in one of the three following categories:

- Fire;
- Explosion;
- Toxic dispersion (affecting humans and/ or the environment).

Effects of dangerous phenomena are also classified in three categories:

- Thermal effects: related to the more or less rapid combustion of a flammable or combustible substance.
- Overpressure effects: resulting from a pressure wave. This can arise, for example, from an explosion, a chemical reaction or violent combustion or a brutal decompression of a pressurised gas (for example, the burst of a bottle of compressed air).
- Toxic effects: resulting from the absorption of a hazardous toxic substance or preparation (chlorine, ammonium, phosgene, etc.), due to a leak on an installation or the release of a toxic substance from a chemical decomposition during a fire or a chemical reaction.

Missile effects may also be considered, i.e. the generation of projectiles when an explosion occurs. However these effects are usually not taken into account for the classification of dangerous substances or in risk assessments: there is a lack of suitable tool for assessing the extent of this effect and the experience shows that in most cases these types of effects have a lower hazard potential than toxic, overpressure or thermal effects.

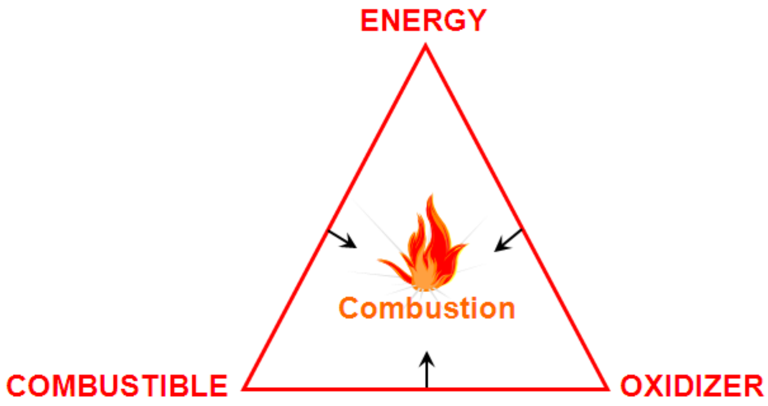
Each dangerous phenomenon and the effects associated are introduced in the following paragraphs. They are considered into more details in Task 2 about the modelling tools.

3.2 Fire

3.2.1 Description

Fire is the rapid oxidation of a material in the exothermic chemical process of combustion, releasing heat, light, and various reaction substances. Three conditions are necessary to trigger and sustain a fire, which can be represented as the fire triangle (cf. Figure 3.1). The triangle illustrates the three elements a fire needs to ignite: heat (or energy), fuel (combustible), and an oxidising agent (usually oxygen). A fire naturally occurs when the three elements are present and combined in the right mixture. Fire can be prevented or extinguished by removing any one of the elements in the fire triangle.

Figure 3.1 Representation of the fire triangle



The most commonly known oxidiser is the oxygen in the air. Ozone, nitrates, or peroxides like hydrogen peroxide constitute other examples of oxidisers.

The combustible is typically a flammable gas, flammable liquid or a flammable solid. The reaction occurs in the gaseous medium around the surface of the liquid or the solid combustible.

Various sources of energy can ignite a fire such as: flame, heat, electrical sparks, sparks from friction, hot surfaces, static electricity, projection from welding and flame cutting.

3.2.2 Different types of fire

In terms of modelling, different kinds of fires are typically distinguished:

- Pool Fire. A pool fire is a fire resulting from the combustion of a pool of combustible for instance in a tank or a basin. It could also be fire of a meltable solid.

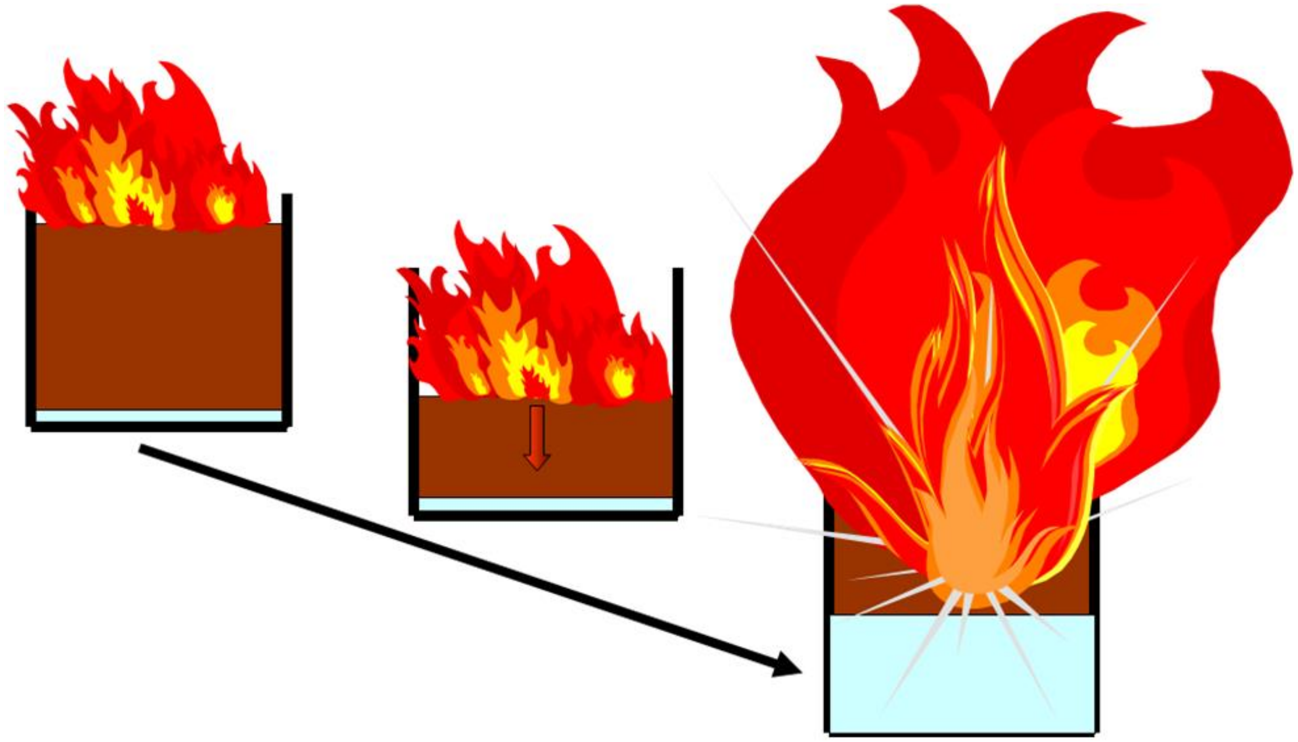
- Self-heating of powder substance. Under certain conditions, some combustible substances stored as powder and in a large storage vessel can generate fire due to a spontaneous combustion. This can be observed for instance during the fermentation process of agricultural substances in a silo.

- Jet fire. A jet fire is an inflammation of a flammable gas spray. It could occur for instance through ignition of an accidental leak of flammable gas or an intentional release of a by-product.

- Flash fire. A flash fire is a sudden, intense fire caused by ignition of a mixture of air and a dispersed flammable substance such as solid (dust for instance), combustible liquid or a flammable gas. It is characterised by high temperature, short duration and a rapidly moving flame front.

- Boil Over (cf. Figure 3.2). Boil over is the formation of a fireball resulting from the thermal effects caused by a fire in storage tanks of certain hydrocarbons. It has generally occurred in petrochemical sites, when a fire is ignited in a floating roof tank. The combustible burns and the heat flux is conducted through the hydrocarbon oil and reaches the water deposit generally present at the bottom of the tank. After a few hours, the rapid vaporisation of the liquid water leads to a projection of the flammable hydrocarbon and can spread the blaze over a wide area (up to a few kilometres). Two kinds of boil over exist: the classical boil over and the thin-layer boil over. In terms of distance, the classical boil over would have higher effects distances than the thin-layer boil-over. The more viscous a substance, the higher the chance to develop a classical boil over: a classical boil over generally occurs for heavy or light crude and fuel oil whereas thin-layer boil over is expected for gas oil and kerosene (Jet A).

Figure 3.2 Schematic representation of a boil over



3.2.3 Effects

A fire generates thermal effects and toxicity effects depending on the nature of the smoke.

It is often the origin of other dangerous phenomena like another fire and/or explosion due to thermal effects. It can also generate ground layer pollution owing to the water used to extinguish the fire.

3.3 Explosion

3.3.1 Description

An explosion is a rapid transformation of a chemical system, with a sudden and rapid release of gas, eventually accompanied by a significant heat emission.

The released energy can be of physical or chemical origin (cf. Figure 3.3).

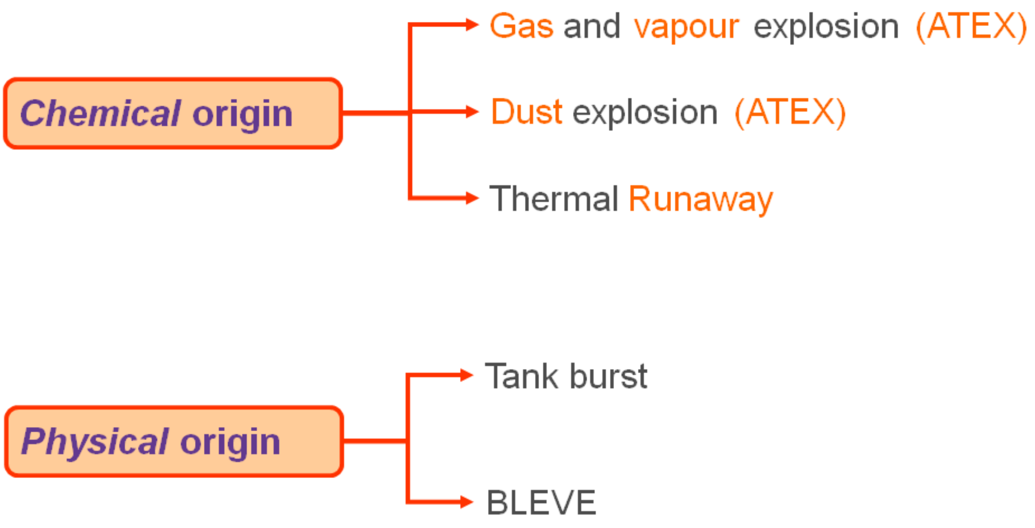
Two types of explosion give rise to a release of energy of physical origin:

- The rupture of a gas pressurised tank;
- The rapid vaporisation of an overheated liquid.

Two types of explosion give rise to a release of energy of chemical origin:

- Explosive atmosphere (combustion reaction – gas, vapour or dust);
- Explosion resulting from a runaway reaction.

Figure 3.3 Different types of explosion



Explosive atmosphere can be caused by flammable gases, mists, vapours or combustible dusts. If there is enough of a substance, mixed with air, it can cause an explosion in the presence of a source of ignition. A hexagon can be used to represent six conditions for an explosion to occur (cf. Figure 3.4):

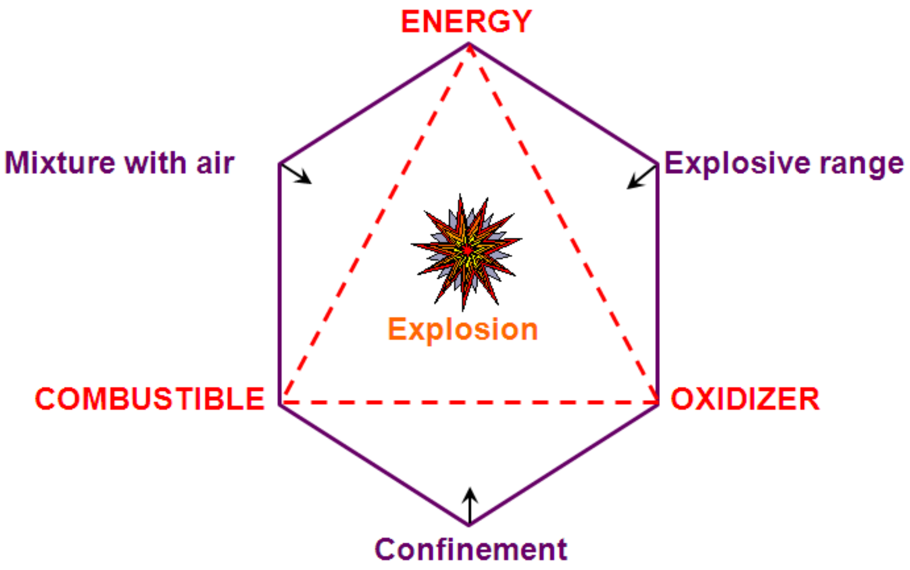
- Conditions represented in the fire triangle, combustible/ oxidiser/ energy, are needed.

- A good mixture between the combustible and the oxidiser is needed. Most of the time, the oxidiser is the oxygen in the air. It can be, for instance, the accidental release of hydrogen in the atmosphere causing the formation of a cloud in the air.

- To have an explosion, it is also necessary that the mixture is inside the explosive range. The explosive range is included between two limits: LEL (lowest concentration of the explosive range at which an explosion can occur) and UEL (upper concentration of the explosive range at which an explosion can occur).

- Confinement is an aggravating factor. In a confined environment the pressure effects would be much higher than in an unconfined area.

Figure 3.4 Hexagon of explosion



Thermal runaway refers to the loss of control of temperature of an exothermic reaction mixture in a vessel. It could be the mixture of two different incompatible substances, but also the decomposition of a thermally unstable substance. Peroxides are well known to decompose releasing a significant amount of energy.

A pressurized gas represents a very important potential source of energy. If this energy is released, it can cause significant effects on the environment. Mechanical rupture can lead to a release of pressure as well as a flammable cloud depending on the gas. In this case an UVCE (unconfined vapour cloud explosion) may occur. Another situation where a pressurised container is caught in fire can lead to a pressure rise reaching the maximal pressure of the vessel.

The BLEVE (boiling liquid expanding vapour explosion) is a specific explosion case caused by the rupture of a vessel containing a pressurised liquid, typically when the vessel is caught within a fire or exposed to thermal radiation from a fire. The pressurised liquid is then heated above its boiling point. The pressure inside the vessel rises to attain the rupture pressure and the following phenomena occur successively:

- Burst of the tank due to the pressure rise;
- Sudden vaporisation of the liquid at ambient pressure;
- Gas cloud explosion (UVCE);
- Fireball due to the inflammation of the residual liquid.

3.3.2 Effects

An explosion generates pressure effects (burst, shock wave, etc.), missile effects (potentially over hundreds of metres), and thermal effects (e.g. fireball and toxic effects, depending on the nature of the substance released).

Generally, explosions are particularly deadly and destructive. They are often the cause of domino effects.

3.4 Toxic dispersion

3.4.1 Description

Toxicology is the science of poisons, which are substances that produce a harmful action on an organism.

The principle of dose was introduced for the first time by Paracelse (16th century): “Everything is poison, nothing is poison. It’s dose that makes a poison”.

The different modes of intoxication are presented in Table 3.1. In terms of major accident scenarios, a rapid impact is considered i.e. acute intoxication.

Table 3.1 Different types of intoxication

Acute toxicity	Strong (concentration) and usually one time dose	Short term exposure
Sub-chronic intoxication	Repeated administration	Medium-term exposure time (several weeks)
Chronic intoxication	Repeated administration	Long-term exposure (from several month to lifetime)

3.4.2 Effects

Toxic dispersion generates toxic effects. The various degrees of toxicity relevant for Seveso are the following:

- Acute toxicity

According to the CLP regulation, acute toxicity refers to adverse effects occurring following oral or dermal administration of a single dose of a substance or a mixture, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours.

- Specific Target Organ Toxicity (STOT) – Single Exposure (SE)

  According to the CLP regulation, STOT (SE) is defined as specific, non-lethal target organ toxicity arising from a single exposure to a substance or mixture. All significant health effects that can impair function, both reversible and irreversible, immediate and/ or delayed are included.

4. List of Parameters and Link with the Dangerous Phenomena

As seen in the previous paragraphs, in the context of risk assessment:

- Three dangerous phenomena are considered: fire, explosion, toxic dispersion.
- Three types of effects are considered: overpressure, thermal and toxic.

Thus, confronting a chemical substance in its context of use, the following questions can be asked:

- Can the substance generate a fire?
- Can the substance generate an explosion?
- Can the substance generate a toxic dispersion?
- Can the substance generate dispersion hazardous for ecosystems?

The answers to these questions are directly linked to the properties of each substance. Table 4.1 summarises the questions related to the research of dangerous phenomena together with the parameters which can help to answer the questions.

Table 4.1 Questions related to dangerous phenomena

	Dangerous phenomena	Key questions regarding a substance	Parameters of the substance	Examples of substance
Can the substance generate a fire?	Pool Fire	Is it flammable/combustible? Is it an oxidiser? Is the substance pyrophoric?	Flashpoint, LFL, UFL, auto-ignition temperature	Solvents
	Self-heating	Is it flammable/combustible?		Coal, storage of cereals in a silo
	Jet fire	Is it a flammable gas?		Rupture of a pipe containing propane
	Boil-Over	Is it a hydrocarbon?	Viscosity	Storage tanks of certain hydrocarbons (fuel oil, gas oil, kerosene)
	Fire ball	Is it flammable/combustible?		
Can the substance generate an explosion?	Vapour cloud explosion	If the substance is flammable/combustible, can it generate an Vapour Cloud Explosion?	P_{vap}, LEL, UEL, K_{st}, K_g, P_{max}, LOC, particles size, humidity rate, MIE	Hydrogen, Methane, Acetylene, combustible dust
	Thermal runaway	Is the substance thermally unstable? Is the substance self-reacting?	Kinetics (Activation energy and pre-exponential factor), ΔT_{ad}, ΔH_r, MTSR, TMR_{ad},	Peroxides, reaction mixture such as polymerization and nitration
	Physical explosion (tank burst)	Is the substance a pressurised gas (risk of tank burst)?	Rupture pressure of the tank	High pressure bottle of nitrogen
	Physical explosion BLEVE	Is the substance a pressurised liquid?	Rupture pressure of the tank, T_{eb}	Butane, propane
	Explosion of explosives	Is the substance an explosive?	Kinetics	Fireworks, nitrocellulose
Can the substance generate a toxic dispersion?	Toxic fumes during a fire, toxic cloud release after an explosion, leak/rupture of equipment	Is the substance toxic (for humans or environment)?	LD_{50} LC_{50}	
Can the substance generate dispersion hazardous for the environment?	Environmental Hazard	Is the substance toxic for the environment?	EC_{50} or LC_{50} NOEC BCF	Carbofuran

For each category, it is important to understand the concept behind each question and each parameter. This is the objective of the following paragraphs. Another important point is to know where to find the information. To be consistent with the CLP regulation, it is assumed that most of the definitions would be extracted from this regulation. If not, the sources will need to be specified. For each property, the regulation also defines a range of tests to classify the substance in different categories as specified above. The tests are not described here in detail but only the principal results obtained.

4.1 Can the substance generate a fire?

To generate a fire, a substance under liquid, solid or gas form, needs to be flammable or pyrophoric.

4.1.1 Definition

According to CLP, a 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 within these two categories:

- Category 1: extremely flammable gas – 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.
- Category 2: flammable gas – gases, other than category 1 which, at 20°C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air.

According to CLP, a flammable liquid means a liquid having a flash point of not more than 60°C within these three categories:

- Category 1: extremely flammable liquid and vapour - flash point < 23°C and boiling point ≤ 35°C
- Category 2: highly flammable liquid and vapour - flash point < 23°C and boiling point > 35°C
- Category 3: flammable liquid and vapour - flash point ≥ 23°C and ≤ 60°C

According to CLP, a flammable solid means a solid which is readily combustible, or may cause or contribute to fire through friction. Readily combustible solids are powdered, granular, or pasty substances or mixtures 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.

According to CLP, an aerosol means aerosol dispenser which are any non-refillable receptacles made of metal, glass or plastics and containing a compressed, liquefied or dissolved gas 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 foam, paste or powder or in liquid state or in gaseous state. Aerosols are considered flammable if they contain any component which is classified as flammable according to the following criteria:

- Liquid with a flashpoint ≤ 96°C, which includes flammable liquids,
- Flammable gases,
- Flammable solids.

According to CLP, a pyrophoric liquid means a liquid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air. Only one category exists: the liquid ignites within 5 minutes when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 minutes.

According to CLP, a pyrophoric solid means a solid substance or mixture which, even in small quantities, is liable to ignite within five minutes after coming into contact with air. Only one category exists: the solid ignites within 5 minutes of coming into contact with air.

Oxidisers are also part of the fire triangle.

According to CLP, a 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. The criteria "more than air does" is further defined as "having an oxidizing power greater than 23.5% as determined by a method specified in the last revision of ISO 10156 and ISO 10156-2".

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

Self-heating substances and mixtures can also cause fire.

According to CLP, a self-heating substance or mixture is a liquid or solid substance or mixture, other than a pyrophoric liquid or solid, which, by reaction with air and without energy supply, is liable to self-heat: this substance or mixture differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after a long period of time (hours or days). Self-heating of substances or mixtures, leading to spontaneous combustion, is caused by reaction of the substance or mixture 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 combustion exceeds the rate of heat loss and the auto-ignition temperature is reached.

4.1.2 Parameters definition

The two criteria used in the CLP regulation are: the flash point and the flammable range.

The **flash point** is the lowest temperature of the liquid, corrected to the standard pressure of 101.3 kPa, at which application of a test flame causes the vapour of the liquid to ignite momentarily and a flame to propagate across the surface of the liquid under the specified conditions of the test. In other terms, flash point is the temperature at which the liquid produces sufficient vapour for combustion to begin. For example, the flash point of fuel oil is 70°C: it has to be heated to 70°C to ignite in the presence of an ignition source.

The **flammable range** of a flammable gas is defined between the "lower flammability limit" (LFL) and the "upper flammability limit" (UFL) in air. The terms "lower explosion limit" (LEL) and "upper explosion limit" (UEL) are often used instead of the LFL and UFL, respectively.

The **“lower flammability limit” (LFL)** is the lowest concentration (of the combustible in air) of the explosion range at which an ignition can occur. The parameter is generally expressed in percentage (%) of combustible in air.

The **“upper flammability limit” (UFL)** is the highest concentration (of the combustible in air) of the explosion range at which an ignition can occur. The parameter is generally expressed in percentage (%) of combustible in air.

As already stated, the combustion reaction which generates a fire occurs in the gaseous medium around the surface of the liquid or the solid combustible. It can also be useful to know two other parameters: vapour pressure and auto-ignition temperature.

The **vapour pressure (P_{vap})** of a liquid is the equilibrium pressure of a vapour above its liquid (or solid). That is, the pressure of the vapour resulting from evaporation of a liquid (or solid) above a sample of the liquid (or solid) in a closed container. It characterises the capacity of a substance to produce vapour above itself. A substance with a high vapour pressure will tend to produce more vapour and for a flammable substance will thus have more chance to reach the lower flammability limit.

The **auto-ignition temperature** of a substance is the lowest temperature at which it will spontaneously ignite in a normal atmosphere without an external source of ignition, such as a flame or a spark.

The **combustion rate** expressed in ($kg.m^{-2}.s^{-1}$) characterises the rate at which the substance burns.

The **heat of combustion** (denoted ΔH_{comb}) is the energy released when a substance undergoes complete combustion with oxygen under standard conditions.

The **surface emissive power of flame** (SEP) expressed in ($W.m^{-2}$) is the thermal heat release rate by unit area of the flame surface.

4.2 Can the substance generate an explosion?

To generate an explosion, different situations are possible:

- The flammable vapour released by a flammable liquid can be accumulated and burn if ignited.
- Dust cloud can potentially explode.
- A flammable gas can burn if ignited.
- A thermally unstable substance reaching its decomposition temperature can generate an exothermic reaction (thermal runaway).
- A highly exothermic reaction between two substances can occur (thermal runaway).
- An explosive can be intentionally or unintentionally used (explosive substances).
- The rupture or a fire surrounding a pressurised gas can occur (physical explosion).

- A Pressurised Liquefied Gas (PLG) pressurised tank surrounded by a fire (BLEVE).

4.2.1 Definition

According to CLP, an explosive substance or mixture is a solid or liquid or mixture of substances which is in itself capable by chemical reaction of producing gas at such temperature and pressure and at such a speed as to cause damage to the surroundings. To characterise an explosive substance or mixture, multiple tests can be performed:

- 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.

To ignite an explosive atmosphere (gas, vapour or dust), it is necessary to be inside the explosive range. Experiments performed in a 20 litre sphere or 1 m^3 chamber can determine the severity of the explosion by measuring the maximum explosion pressure (P_{max}) and the maximum rate of explosion pressure rise (K_{st} for dust clouds and K_g for gas and vapour clouds). For dust, particle size is also an important parameter. If the particles size distribution is too big, the cloud will not explode. The dust must be small enough. It is generally assumed that for a size distribution greater than 500 µm, the chances of a dust explosion is low. The humidity rate is also a parameter which has to be taken into account. Indeed, the more the powder or the dust is dry, the greater the chance that it explodes when dispersed as a cloud.

For thermally unstable substances, it is important to know the decomposition temperature of the substance.

When two incompatible substances are mixed willingly (in a reactor for instance) or by mistake, the exothermic reaction can lead to thermal runaway, which means the loss of control of the temperature. The consequences are generally a pressure rise, the container bursting or the rupture disk opening with the release of a two phase flow mixture. This vented mixture can be toxic. In this case, a blow down and or a scrubber are necessary to neutralise it. This was exactly the situation in the Seveso accident (1974): a thermal runway occurred during the weekend resulting in a pressure rise and an opening of the rupture disk directly connected to the roof, releasing dioxin all over the city. In thermal studies, six parameters are very important to determine: reaction enthalpy, heat capacity, kinetic of the reaction, maximum temperature of the reaction synthesis (MTSR), adiabatic temperature rise (ΔT_{ad}) and time to maximum rate in adiabatic condition (TMR_{ad}).

4.2.2 Parameters Definition

According to the definition provided in the EN 13237 standard, **explosion range** is the range of concentration of a flammable substance or mixture of substances in air, within which an explosion can occur, determined under specified test conditions. In other words it is the percentage of gas that must be present in the air for an explosion to occur. For example: hydrogen’s explosion range is between 4% and 75%, ethylene oxide’s explosion range is between 3.5% and 100% and acetone’s explosion range is between 2.6% and 13%. Hydrogen and ethylene oxide have very large explosion ranges and are therefore very dangerous.

According to the definition provided in EN 13237, the **“lower explosion limit” (LEL)** is the lowest concentration (of the combustible in air) of the explosion range at which an explosion can occur.

According to the definition provided in EN 13237 standard, the **“upper explosion limit” (UEL)** is the highest concentration (of the combustible in air) of the explosion range at which an explosion can occur.

According to the definition provided in EN 13237, the **“limiting oxygen concentration” (LOC)** is the maximum oxygen concentration in a mixture of a flammable substance and air or an inert gas, in which an explosion will not occur, determined under specified conditions. This value is often used to determine the conditions to create an inert atmosphere.

Minimum ignition energy (MIE) is the minimum amount of energy required to ignite a combustible vapour, gas or dust cloud, for example electrostatic discharge. The MIE of hydrogen is 17 microjoules, the MIE of ethanol is 70 microjoules and the MIE of methane is 300 microjoules. It takes only a spark to cause hydrogen and ethanol to explode. A spark of 17 microjoules is so small that it is often invisible. Sparks are produced a thousand times more powerful just by walking on a carpet or dropping a tool from a bench.

The **heat of combustion** (denoted ΔH_{comb}) is the energy released when a substance undergoes complete combustion with oxygen under standard conditions.

The **decomposition temperature** of a substance is the temperature at which the substance chemically decomposes. At this temperature the chemical bounds can be broken and incondensable gases (CO_2, H_2, CH_4, N_2...) can be generated.

Adiabatic conditions refer to conditions where there is no transfer between the thermodynamic system and the surroundings. It means that all the energy released by an exothermic reaction is accumulated inside the system.

The **standard enthalpy of reaction** (denoted ΔH_r) is the enthalpy change that occurs in a system when one mole of matter is transformed by a chemical reaction under standard conditions. It expresses the energy released by the reaction during the chemical transformation of the molecules. It is expressed in (J/mol) or (J/g).

The **heat capacity or thermal capacity** (denoted C_p) of a defined system is the amount of heat (usually expressed in calories, kilocalories, or joules) needed to raise the system's temperature by one degree (usually expressed in Celsius or Kelvin). It expresses the capacity of a system to absorb heat. It is expressed in (J/(g.K)).

The **kinetic of the reaction** is an expression which expresses the evolution of the reaction over time (reaction rate). It is expressed in (mol/(L.s)). When tests are performed in pseudo-adiabatic calorimeters, rates can reach 200°C/min and 5,000 kPa/min for a very highly exothermic reaction.

The **adiabatic temperature rise (ΔT_{ad})** is the temperature rise due to the principal reaction under adiabatic conditions.

The **maximum temperature of the reaction synthesis (MTSR)** is the maximum temperature reached in the process due to the principal reaction under adiabatic conditions during a thermal runaway. Thus MTSR is calculated by adding ΔT_{ad} to the process temperature. For instance, if the process is carried out at 50°C and the ΔT_{ad} equals 100°C, the MTSR would reach 150°C. It provides very useful information for the evolution of the system in case of thermal runaway: the higher the temperature, the more dangerous the situation is. By reaching 150°C, the reaction mixture can boil and the pressure can rise. A high MTSR is also a risk to start secondary reactions or decomposition reactions which can also be exothermic and hazardous.

The **time to maximum rate in adiabatic condition (TMR_{ad})** is the time between the time where the MTSR is reached and the time when the thermal explosion occurs. It is important to know the kinetic of the phenomena and the time left after the thermal runaway has begun: if TMR_{ad}=24h for instance, it indicates that in case of failure there is time to take actions to limit the development of the runaway; if TMR_{ad}=10 min, there is likely to be no action possible on the process (in case of failure) to stop the thermal runaway.

4.3 Can the substance generate a toxic dispersion?

In a major accident context, toxic effects are generally the result of a fire or an explosion. They can also be the consequence of a leak/ rupture. As with other hazards related to chemicals, “toxic” is an intrinsic property.

4.3.1 Definition

According to CLP, acute toxicity means those adverse effects occurring following oral or dermal administration of a single dose of a substance or a mixture, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours. The hazard class acute toxicity is differentiated into: acute oral toxicity, acute dermal toxicity and acute inhalation toxicity. Acute toxicity values are essentially expressed as (approximate) LD_{50} (mg/kg) (oral, dermal) or LC_{50} (ppm or mg/L) (inhalation).

According to CLP, specific target organ toxicity (single exposure) (STOT-SE) is defined as specific, non-lethal target organ toxicity arising from a single exposure to a substance or mixture. All significant health effects that can impair function, reversible and irreversible, immediate and/ or delayed are included. However the effects listed below, are assessed separately and consequently are not included in the specific target organ toxicity (single exposure) (STOT-SE) class: acute toxicity, skin corrosion/ irritation, serious eye damage/ eye irritation, respiratory or skin sensitisation, germ cell mutagenicity, carcinogenicity, reproductive toxicity and aspiration toxicity.

4.3.2 Parameters

LD$_{50}$ (median lethal dose): is a statistically derived single dose of a substance that can be expected to cause death in 50% of animals (e.g. rat for acute oral and inhalation toxicity studies, and rabbit, rat or guinea pig for dermal toxicity studies) when administered by the oral or dermal route. The LD$_{50}$ value is expressed in terms of weight of test substance per unit weight of test animal (mg/kg).

LC$_{50}$ (median lethal concentration): is a statistically derived single concentration of a substance that can be expected to cause death in 50% of animals when administered by the inhalation route during 4 hours. The LC$_{50}$ value is expressed in terms of ppm or mg/m^3.

4.3.3 Scope for Seveso III

According to Annex I of the Seveso III Directive and the CLP regulation, a substance or a mixture falls under the scope of Seveso if:

- Oral LD$_{50}$ < 50 mg/kg (i.e. acute toxic – Category 1 and Category 2), or
- Dermal LD$_{50}$ < 200 mg/kg (i.e. acute toxic – Category 1 and Category 2), or
- Inhalation LC$_{50}$ for gaseous chemicals < 2500 ppm (i.e. acute toxic – Category 1, Category 2 and Category 3), or
- Inhalation LC$_{50}$ for vapour chemicals < 10 mg/L (i.e. acute toxic – Category 1, Category 2 and Category 3), or
- Inhalation LC$_{50}$ for mist/dust chemicals < 1 mg/L (i.e. acute toxic – Category 1, Category 2 and Category 3), or
- Chemicals classified in the first category of the "specific target organ toxicity (single exposure) (STOT-SE)" class. Guidance value ranges for single-dose exposure which has produced a significant non-lethal toxic effect are those applicable to acute toxicity testing (see above), as indicated in CLP. Indeed, acute toxicity studies can include clinical observations and detailed macroscopic and microscopic examination to enable the toxic effects on target tissues/organs to be identified.

4.4 Can the substance generate a dispersion hazardous for the environment?

Environmental hazard is linked to intrinsic properties of the substance: (eco) toxicity, potential for bioaccumulation and for degradability.

4.4.1 Definition

According to CLP, acute aquatic toxicity is the intrinsic property of a substance to be injurious to an aquatic organism in a short-term aquatic exposure to that substance.

Chronic aquatic toxicity means the intrinsic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which are determined in relation to the life-cycle of the organism.

According to CLP bioaccumulation means the net result of uptake, transformation and elimination of a substance in an organism due to all routes of exposure (i.e. air, water, sediment/soil and food). Bioaccumulation of substances within aquatic organisms can give rise to toxic effects over longer time scales even when actual water concentrations are low.

Degradation means the decomposition of organic molecules to smaller molecules and eventually to carbon dioxide, water and salts.

4.4.2 Parameters

EC_{50} or LC_{50} are statistically derived single concentrations of a substance that can be expected to cause 50% of the observed effect (in crustaceans or plants, EC_{50}) or death in 50% of fish (LC_{50}). Acute aquatic toxicity is determined using a fish 96 hour LC_{50}, a crustacea species 48 hour EC_{50} and/or an algal species 72 or 96 hour EC_{50}. These species cover a range of trophic levels and taxa and are considered as surrogate for all aquatic organisms.

NOEC or other equivalent L(E)Cx (e.g. EC_{10}) is the highest concentration of toxicant to which organisms are exposed in a full life-cycle or partial life-cycle (short-term) test, that causes no observable adverse effects on the test organisms.

The **octanol/ water partition coefficient**, usually reported as a log K_{ow}, can be used to determine the potential for bioaccumulation of organic substances. The relationship between the log K_{ow} of an organic substance and its bioconcentration as measured by the **bioconcentration factor** (BCF) in fish has considerable scientific literature support. Using a cut-off value of log $K_{ow} \geq 4$ is intended to identify only those substances with a real potential to bioconcentrate. While this represents a potential to bioaccumulate, an experimentally determined BCF provides a better measure and should be used in preference if available. A BCF in fish of ≥ 500 is indicative of the potential to bioconcentrate.

Substances that rapidly degrade can be quickly removed from the environment. While effects of such substances can occur, particularly in the event of a spillage or accident, they are localised and of short duration. In the absence of rapid degradation in the environment a substance in the water has the potential to exert toxicity over a wide temporal and spatial scale. According to CLP, substances are considered rapidly degradable in the environment if one of the following criteria holds true:

(a) If, in 28-day ready biodegradation studies, at least the following levels of degradation are achieved;

(i) Tests based on dissolved organic carbon: 70 %
(ii) Tests based on oxygen depletion or carbon dioxide generation: 60 % of theoretical maximum.

These levels of biodegradation must be achieved within 10 days of the start of degradation which is taken as the time when 10 % of the substance has been degraded; or

(b) If, in those cases where only BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) data are available, when the **ratio of BOD/COD** is ≥ 0.5; or

(c) If other convincing scientific evidence is available to demonstrate that the substance can be degraded (biotically and/or abiotically) in the aquatic environment to a level > 70 % within a 28-day period

4.4.3 Scope for SEVESO III

According to Annex I of the Seveso Directive and the CLP regulation, a substance or a mixture falls under the scope of the Directive if:

- 96 hr LC_{50} / 48 hr EC_{50} / 72 or 96 hr EC_{50} < 1 mg/l (i.e. hazardous to the aquatic environment in Category Acute 1 or Chronic 1), or
- 96 hr LC_{50} / 48 hr EC_{50} / 72 or 96 hr EC_{50} < 10 mg/l (i.e. hazardous to the aquatic environment in Category Chronic 2).

4.4.4 Long-term effects due to accidental dispersion of persistent, bioaccumulative and toxic pollutants

Special attention has to be given to substances which are persistent, bioaccumulative and toxic and which may be subject to long range transport. A single release of these chemicals may result in long-term effects on ecosystems, affecting the entire trophic network and thus, the structure and function of the ecosystems.

The dispersion of these substances, such as dioxins, in ecosystems may result from unintentional releases. Hence, these substances are out of the scope of Seveso III. However, it seems interesting to underline that the criteria for identification of these substances are set out in Annex XIII to regulation 1907/2006 (REACH) and in regulation 850/2004 which implements the UN Stockholm Convention on Persistent Organic Pollutants.

5. Synthesis of Part 1

As seen in the previous paragraphs:

- Three dangerous phenomena are considered: fire, explosion, toxic dispersion.
- Three types of effects are considered: overpressure, thermal and toxic.

Thus, confronting a chemical substance in its context of use, the following questions can be asked:

- Can the substance generate a fire?
- Can the substance generate an explosion?
- Can the substance generate a toxic dispersion?
- Can the substance generate a dispersion hazardous for the environment?

The answers to these questions are directly linked to the properties of each substance, presented in the sections above. The table below (Table 5.1) summarises the links that can be made between the inherent properties of a substance and the dangerous phenomena which may be generated.

The colour code is to be understood as follows:

▨	General inherent properties
□	Properties relevant to the generation of a fire / an explosion
■	Properties relevant to the generation of a toxic dispersion / a dispersion hazardous for the environment

Table 5.1 Parameters used to characterise the dangerous phenomena

Inherent properties	Notation	Unit	Dangerous phenomena
Adiabatic temperature rise	ΔT_{ad}	°C	Thermal runaway
Auto-ignition temperature	AIT	°C	Explosive atmosphere
Bioaccumulation	--	--	Hazardous dispersion for ecosystem
Boiling point	T_{eb}	°C	All
Concentration Dose	LC_{50}	ppm or mg/L	Acute toxicity and chronic aquatic toxicity
Combustion rate	r_{comb}	$kg.m^{-2}.s^{-1}$	Pool fire
Decomposition temperature	$T_{decomposition}$	°C	Thermal runaway
Enthalpy of reaction	ΔH_r	$J.kg^{-1}$	Thermal runaway
Explosion range	LEL - UEL	% volume	UVCE – Explosive atmosphere
Flammable range	LFL - UFL	% volume	Fire
Flash point	FP	°C (for liquids)	Fire - Explosion
Granulometry	G	% (size distribution)	Dust Explosion
Heat capacity	C_p	J/(g.K)	All – Thermal runaway
Heat of combustion	ΔH_{comb}	$J.kg^{-1}$	UVCE - Explosive Atmosphere - Jet fire - Pool fire
Humidity rate	$\tau_{humidity}$	%	Explosive atmosphere
Lethal Dose, 50%	LD_{50}	mg/kg	Acute toxicity
Limiting oxygen concentration	LOC	% volume	Used to define the inerting conditions

Inherent properties	Notation	Unit	Dangerous phenomena
Mass density	ρ	$kg.m^{-3}$	All - UVCE
Maximum temperature of the reaction synthesis	MTSR	°C	Thermal runaway
Melting point	T_m	°C	All
Minimum ignition energy	MIE	J	Explosive atmosphere
Molar mass	M	g/mol	All
No Observed Effect Concentration	NOEC	concentration of toxicant to which organisms are exposed in a full life-cycle or partial life-cycle	Hazardous dispersion for ecosystem
Severity of the explosion	K_g	$bar.m.s^{-1}$	Explosive atmosphere
Solubility	s	g of solute in g of solvent	Mixture characteristic
Surface emissive power of flame	SEP	$W.m^{-2}$	Pool Fire
Surface tension	γ or σ	mN/m	Intrinsic property
Time to maximum rate	TMR_{ad}	s	Thermal runaway
Vapour pressure	P_{vap}	Pa or bar	All
Viscosity	η	cP	Intrinsic property

Part 2

Initial Screening

1. Introduction

This part aims at providing the concrete steps that could be undertaken by the member states as part of the initial screening stage. Member states could follow one, two or the totality of the steps described in the sections below. Applying all steps would allow the member states to cover each of the key physicochemical properties highlighted in the first part of this task to draw conclusions on the ability to cause dangerous phenomena in relation to those properties.

The objective of the initial screening is to eliminate those substances for which a potential for major accident hazard clearly exists. It aims at identifying whether a certain substance, based on its key physicochemical properties, could cause a release of matter or energy that could create a major accident. If it is clear from this initial screening that the substance has the potential to create a major accident, the process would be ended at this stage. If it is unclear, the assessment could be taken to the next step i.e. more detailed assessment. It is important to highlight that this initial screening does not aim at definitively identifying substances which could not generate a major accident, and then which could be excluded from the scope of Seveso III.

This stage is to be an initial screening by the member state responsible for the notification, in order to decide whether to take it to the next step. It requires only limited information and covers the characteristics mentioned in Article 4(1)(a) to (c) and using the information referred to in Article 4(3)(a) to (f).

2. First step: Seveso III scope

It seems important to highlight that the substance under assessment should belong within the scope of the Seveso III Directive. The first step of the initial screening consists of checking whether the candidate substance belongs to one or several hazard categories listed in Part 1 of Annex I of Seveso III, which are in accordance with the CLP regulation. Moreover, it should be checked that the candidate substance is not a named substance listed in Part 2 of Annex I of Seveso III, for which no exclusion is conceivable.

This step seems self-evident but it would help to ensure that time is not wasted in pursuing inappropriate cases. It only requires listing the CLP hazard categories under which the substance is classified and checking whether one or several categories are listed in Part 1 of Annex I of the Seveso III. If not, the substance is out of scope and the assessment stops.

If the substance belongs to at least one hazard category listed in Part 1 of Annex I of Seveso III, it can go through the second screening level. It would also be appropriate at this stage to check e.g. whether the case in question concerns a mixture and whether the concentration of the substance in the mixture would lead to inclusion in Part 1 of Annex I.

3. Second Step: Analysis of Past Accidents and other Assessments

3.1 Past accidents

After having checked that the substance under assessment falls under the scope of Seveso III, a second level of screening would consist of checking whether or not the substance has already been implied in a major accident:

- Those substances that have already been involved in a major accident, with no more specific mitigating factors now (e.g. packaging) than there was at the time of the accident, can directly be eliminated from the assessment methodology.

- Those substances that have been implied in a major accident but which today are regulated at EU scale to be stored/ handled in different conditions could warrant further assessment.

A non-exhaustive list of major accidents databases that should be checked include ARIA (Ministry of Ecology, Sustainable Development, Energy, France) and eMars (EU), which contain respectively worldwide and European accidents, and which are presented in the Task 4 report. The MHIDAS database (HSE, UK) also provides information on incidents involving hazardous materials that result in or have the potential to produce off-site impact. Other databases include RIDDOR (HSE, UK), I-NET (Ministry of Social Affairs and Employment, the Netherlands), FACTS (TNO, the Netherlands) and Hazards Intelligence (Ility, Finland).

A difficulty at this stage relates to the uncertainties and/ or lack of data recorded in the accident databases. Only fragmented information may be provided, which may constitute an obstacle to interpreting the potential role of the substance under assessment in the occurrence of the event.

3.2 Review of other assessment studies of the substance

The analysis of past accidents could be complemented by the consideration by member states of other safety assessments identifying potential for major accident hazard. For example, this could consider whether safety reports for any of the Seveso establishments holding the substance (e.g. in the member state concerned), or other known assessments, have identified credible accident scenarios leading to conclusion of the potential for major accident hazard involving the substance. If they have, this is probably a good sign that the assessment should be ended at this initial screening stage. If not – or if there are particular mitigating factors such as packaging – then further assessment could be warranted.

If the substance under assessment goes through the two previous steps, it seems appropriate at this stage to collect basic information on the substance, particularly relevant information referred to under Article 4(3) focusing on readily available data (i.e. excluding detailed information where not readily available e.g. injury to fatality ratio, substance-specific operating conditions – this would be collected as part of the main assessment, after the initial screening). This information is covered in the first part of Task 1. Data may include e.g. physicochemical properties (molecular mass, vapour pressure, melting point, boiling point, reactivity, viscosity, water solubility);

health hazard data e.g. effects concentrations/doses; environmental hazard data e.g. LC_{50} values; physical hazard data e.g. flammability.

4. Third Step: Index Approach

4.1 Generalities

This stage consists of ranking the potential for major accident hazard of the substance under assessment in relation to a similar substance (i.e. a substance having similar physicochemical properties and belonging to the same hazard category), or selection of other substances, based on the properties of those substances. These "reference" substances could be named substances listed in Part 2 of Annex I of Seveso III (see Section 4.2 for further guidance). If it is evident that the potential for major accident hazard of the substance under assessment is equal to or higher than the "reference" substance (or groups of substances), then it can be eliminated from the assessment methodology unless there are identified reasons why further analysis should be undertaken (see Section 5). If the comparison shows potentially lower accident potential than these reference substances, it is worthwhile proceeding to a more detailed assessment.

It is envisaged that this approach could be done by using one of a number of ranking/ index methods. It is not considered appropriate for this report to specify what the specific reference substances should be (as relevant reference substances will be determined by the characteristics of the substance under assessment), but the source documents for a number of relevant methods include examples. Possible methods, widely recognised and used for different purposes, could include:

- Ranking methods for the **acute toxicity aspects of the potential for major accident hazard** of chemicals have been reviewed in Wilday (2010)[11]. Health hazard indexes highlighted in this document could be used in order to compare the potential for major accident hazard of the substance under assessment and the reference substance(s) as regard to health hazards.

These take into account properties such as vapour pressure, melting point and molecular weight, as well as readily available data on acute LC_{50} values. The indexes developed have been generated for a number of substances already included within the scope of Seveso, in terms of the "comparative footprint" of accidents, which was estimated for the selected substances that are already in Seveso Annex I (using PHAST modelling in a specific study[12]).

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[11] Wilday J, Trainor M, Allen J, Hodgson R, 2010, Development of a hazard index method to rank human acute toxicity aspects of major accident potential (not yet submitted).

[12] Trainor, M.T., Wilday, A.J., Moonis, M., Rowbotham, A.L., Saw, J.L., Bosworth, D.A., 2008. Adapting the EU Seveso II Directive for GHS: initial UK study on acute toxicity to people, in Safety, Reliability and Risk Analysis: Theory, Methods and Applications, Martorel et al. (eds) 2008 vol. 3 p 2353-2361 ISBN 978-0-415-48513-5.

It is recognised in the paper that the PHAST model only includes a limited number of defined substances, so use of this index method would provide a quick basis for comparison where the substance under assessment is not included as a defined substance in the model.

- As regards **physical hazards**, the most widely used hazard index is the Dow Chemical Company's Fire and Explosion Index (the Dow Index)[13]. A factor of this index may be used to rank the physical hazard potential of the substance under assessment and the reference substance(s).

- In terms of **environmental aspects**, a number of index methods were reviewed in the report on Task 3, such as the Czech H&V index and the Swedish Environment Accident Index. These could potentially be used to compare the relative scale of environmental impacts for the substance under assessment with other Seveso substances with (known) potential for generating a major accident.

Use is made of the information provided in the first part of this task. These indexes could provide a means of undertaking a rapid screening of a substance to compare with other Seveso substances. The results should not be treated as definitive but may provide a useful indication as to whether to proceed to more detailed assessment.

Note that the index approaches introduced above enable one to (crudely) assess the potential for a major accident involving a substance considering each hazard category separately. The potential for combination of hazards is generally not taken into account in these approaches. It could be possible that for each of the hazard categories of the substance in question, the major accident potential is lower than that of the chosen reference substance, but that as a whole its hazard categories do indicate potential for a major accident. As a result showing that potential for major accident regarding each hazard category is lower for the substance being assessed than for the reference substance is not sufficient on its own to rule the substance out. Therefore, such issues should be taken into account when applying these methods

4.2 Guidance on the choice of the reference substance(s)

As underlined above, it does not seem appropriate for this report to specify what the specific reference substances should be. However, some guidance on the choice of the reference substance(s) is provided in this section.

The substance under assessment belongs to a number of hazard categories under the CLP regulation, some of which are relevant under Seveso III (i.e. listed in Part 1 of Annex I of the Directive). It is suggested to find one or several reference substances that meet the following criteria:

- The reference substance should broadly have similar chemical and physical properties (e.g. one should not compare liquids with solids).

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[13] AIChE, 1994, Dow's Fire & Explosion Index Hazard Classification Guide. Lees F.P., Loss Prevention In The Process Industries – Hazard Identification, Assessment and Control, Volume 1, 2nd Edition

- The reference substance(s) belong(s) to the same Seveso III hazard categories as the substance under assessment. There could be as many reference substances as Seveso III hazard categories of the substance under assessment, or one reference substance could be suitable for all the hazard categories.

- The reference substance(s) is a named substance listed in Part 2 of Annex I of the Directive whose threshold has been changed as compared to the ones in Part 1 of Annex I.

If several substances meet these criteria, it is suggested that the one with the highest threshold quantity be chosen (i.e. the potentially less harmful one) in order to be conservative when the comparison with the substance under assessment is to be made. This guidance is summed up in Table 4.1, which can be used as a tool to choose the reference substance.

The third step of the initial screening allows comparison of the substance under assessment with certain reference substances. However, the scope of comparison is limited to named substances in Part 2 of Annex I of Seveso, and does not cover the wider range of substances that have potential for major accident hazard but which are not listed in Part 2 of Annex I. Nevertheless, the aim of this part of the assessment is a screening process, which is not sufficient to draw definitive conclusions on the impossibility for the substance under assessment to generate a major accident.

Moreover, it seems important to highlight that it may be difficult to choose reference substances that are agreed upon by all stakeholders. Again, as this is only a screening stage, more detailed assessment would be required later on in the process, so definitive conclusions at this stage are not necessary.

Table 4.1 Material to guide the choice of the reference substance

List of hazard categories of the substance under assessment relevant under Seveso III	List of potential candidates for reference substances and associated thresholds	Reference substances chosen
Health hazards	[Member States to complete]	
Physical hazards		
Environmental hazards		

4.3 Acute toxicity aspects

4.3.1 Background

The indexes presented in this section have been reviewed by Wilday (2010). They were originally developed for a regulatory purpose and helped inform the incorporation of the new Globally Harmonised System of chemical classification into defining the scope of the Seveso Directive.

4.3.2 Liquids

Index 1 highlighted in Wilday (2010) indicates the **propensity of the substance to vaporise** and thereby be available for inhalation exposure.

Index $1_{liquids} = P_{vap}/ 4hrLC_{50}$

Where P_{vap} is the vapour pressure at ambient temperature (bar) and the 4 hour LC_{50} is the concentration which will kill 50% of a sample by inhalation with an exposure of 4 hours (mg/litre).

Index 2 is derived from the Lacoursiere method (in Wilday, 2010) and expresses the substance's potential to become airborne and disperse. In the Lacoursiere method, physical form and volatility were combined with a measure of toxicity (level of concern) to produce an overall risk "ranking factor" defined as:

$\text{Index}_{Lacoursiere}$ = Level of concern/V

Where V is the index of **potential to become airborne and disperse**.

For liquids, $V = (1.6 \times MW^{0.67}) / (T_{eb} + 273)$

Where MW is the molecular weight (grammes/mole) and T_{eb} is the boiling temperature in degrees Celsius.

Although Lacoursiere used the US National Institute for Occupational Safety and Health IDLH (Immediately Dangerous to Life or Health) data as the level of concern, Wilday's work used the 4 hour LC_{50} (in mg/litre) instead since data were more readily available for a large number of substances. To be consistent with Index 1, Index 2 may be expressed as follows:

Index $2_{liquids} = ((1.6 \times MW^{0.67})/(T_{eb} + 273)) / 4hr\ LC_{50}$

Where MW is the molecular weight (grammes/mole) and T_{eb} is the boiling temperature in degrees Celsius.

4.3.3 Gases and solids

Wilday (2010) underlines that V has been set to 1 for gases and solids in the Lacoursiere method, meaning that all of a substance once released can potentially become airborne. This is clearly the case for gases. For solids, it might also be the case if:

- The solid is present as a finely divided dust; or
- The solid is involved in a fire (potentially giving rise to vapour and/ or entrained solids of the substance itself, together with combustion products which may be more or less toxic than the original substance).

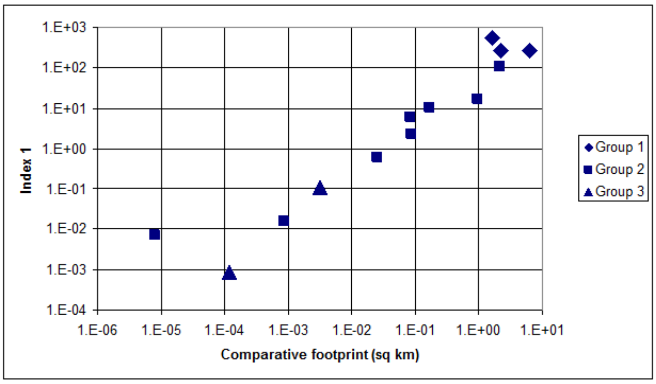
As a result, the index for gases and solids is the following:

$\text{Index}_{\text{gases-solids}} = 1/ \text{4hr } LC_{50}$

However, the development of an index for solids is unlikely to be productive since the potential for acute toxicity major hazards is dominated by site-specific factors including the particle size and packaging.

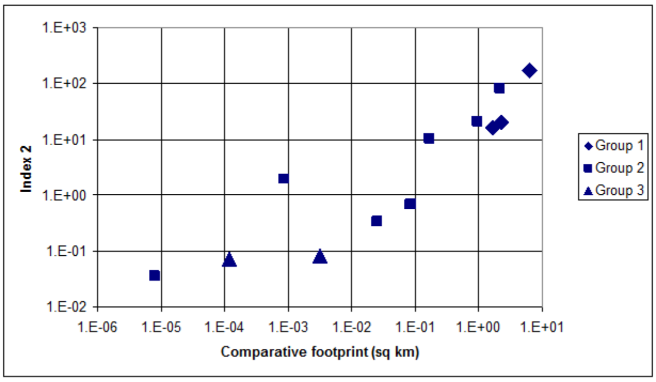
Wilday (2010) shows the results of plotting these proposed indexes versus comparative footprint for a range of different substances for F2 weather conditions (stability category F and 2 metres per second wind speed – this is typical of still night-time conditions). The comparative footprints were calculated for a number of substances using the commercially available consequence modelling software package PHAST version 6.5 (see Task 2). It can be seen from Figure 4.1 and Figure 4.2 that there is a reasonable correlation between comparative footprint and both Index 1 and Index 2.

Figure 4.1 Index 1 (vapour pressure divided by 4hLC50) as a function of comparative footprint



Source: Wilday, 2010

Figure 4.2 Index 2 as a function of comparative footprint



Source: Wilday, 2010

4.4 Physical aspects

The hazard potential of a substance regarding physical aspects (i.e. explosion and combustion) may be determined using a factor of the widely recognised Dow Chemical Company's Fire and Explosion Index (the Dow Index: F&EI). The F&EI calculation is a tool to help determine the areas of greatest loss potential in a particular process, and its original purpose was to serve as a guide to the selection of fire protection methods. It has been developed by the Dow Chemical Company in cooperation with the American Institute of Chemical Engineers.

The computation of this index is completely described in Dow's Fire & Explosion Index Hazard Classification Guide. F&EI is calculated as follows:

$\text{F\&EI} = M_F \text{ x PUHF}$

Where:

- M_F (material factor) is a measure of the intrinsic rate of potential energy release from fire or explosion produced by combustion or chemical reaction. In other words, it is a measure of the potential energy release from the material.

- PUHF (process unit hazards factor) is the product of a penalty factor (i.e. factor reflecting the potential for development or escalation of an incident that could cause a fire or an explosion) for general process hazards and a penalty factor for special process hazards. These penalty factors are process / site-specific.

In the context of Article 4, the M_F could be used as an index that enables comparison of the potential for major accident hazard in terms of physical hazards of the substance under assessment with a reference substance. The M_F is obtained by considering two components: the flammability and the reactivity (or instability) of the substance. It has a value range of 1-40. Use is made respectively of the NFPA (National Fire Protection Agency) fire rating N_F and reactivity rating N_R, as illustrated in the table below (Table 4.2). If the material is a combustible dust, the Dust Hazard Class Number (S_t number) is used rather than the N_F.

Table 4.2 Dow F&EI: Material Factor determination guide

		Reactivity or Instability				
Liquids & Gases Flammability or Combustibility	**NFPA 325 M or 49**	**NR = 0**	**NR = 1**	**NR = 2**	**NR = 3**	**NR = 4**
Non-combustible	$N_F = 0$	1	14	24	29	40
F.P. > 93.3°C	$N_F = 1$	4	14	24	29	40
F.P. > 37.8°C ≤ 93.3°C	$N_F = 2$	10	14	24	29	40
Combustible Dust or Mist						
St-1 (K_{st} ≤ 200 bar m/sec)		16	16	24	29	40
St-2 (K_{st}= 201-300 bar m/sec)		21	21	24	29	40
Combustible Solids						
Dense > 40 mm thick	$N_F = 1$	4	14	24	29	40
Open < 40 mm thick	$N_F = 2$	10	14	24	29	40
...						

F.P.: Flash Point, closed cup

Source: Table extracted from the Dow's Fire & Explosion Index Hazard Classification Guide

First, the parameters shown in the left column of the table have to be determined. The N_F of liquids and gases is obtained from flash point data, and the S_t of dusts or mists is determined by dust explosion testing. The N_F of combustible solids depends on the nature of the material as categorised in the left column. These are readily available data (see first part of this task). Moreover, N_F of a number of substances may be found in NFPA 325M, NFPA 49 or Appendix A of the Dow guide.

The reactivity value (N_R) can be obtained from a qualitative description of the instability (or reactivity with water) of the substance at ambient temperature, described in NFPA 704. N_R can also be obtained by looking at the exotherm start, which is the temperature at which a heat-generating chemical reaction is first detected in a calorimeter. The exotherm start could be considered as the combination of the decomposition temperature and the enthalpy of reaction described in the first part of this task. However, these properties are not readily available. They are obtained through experimental tests, which are not likely to be appropriate in the context of the initial screening of the assessment methodology. Like N_F, the N_R of a number of substances may be found in NFPA 325M, NFPA 49 or Appendix A of the Dow guide.

It should be noted that the base M_F is a measure of the hazard of the substance at ambient temperature and pressure. If these are not the conditions applying, the base M_F needs to be adjusted (see the Guide for more information).

In case of mixtures, usually the substance with the highest M_F, which is of significant concentration (about 5%), should be used as the basis for the M_F.

The use of this index does not seem straightforward in the context of Article 4 since some information may not be readily available to calculate the reactivity value. It is then suggested that if the substance under assessment and the reference substance are listed in NFPA 325M, NFPA 41 or Appendix A of the Dow guide, the M_F could be used to compare the physical hazard potential of both substances. Otherwise, relying solely on the N_F of the substance (i.e. its flash point and boiling point, as explicated in the first column of Table 4.2) could constitute an alternative solution.

It seems that no other index methods for physical hazards are as complete as the F&EI presented above.

4.5 Environmental aspects

A number of index methods for the environment are mentioned in the Task 3 report. An example of the use of one such method is provided below. Other methods may be more appropriate depending on the substance under consideration in the context of Article 4.

Among the steps required to determine the Czech Hazard and Vulnerability Index (H&V Index) presented in the Task 3 report, the step of calculating the index of toxic hazard of a specific substance is to be undertaken, and more specifically the computation of an index of hazard to the water environment. In the context of Article 4, this index is of interest as it may be used to compare the environmental hazard potential of two substances. In this context, and in most of the approaches discussed in the context of the Seveso Directive, the environmental hazard potential is assessed according to the potential for ecotoxicological effects. It should also be borne in mind that effects upon the quality of drinking water may also be important in determining whether a major accident can occur as effects on human health may be significant. Indeed, the interruption of drinking water is identified in the Annex VI of

Seveso III as a criterion for notifying a major accident to the Commission. These should be taken into account at the initial screening stage and also when undertaking more detailed assessment.

Index of hazard to the water environment is defined according to two parameters: Code A (toxicity) and Code B (physical properties), which are defined in tables presented in the Task 3 report. The index of toxic hazard is then defined by the sum of the A and B codes, as illustrated in the Task 3 report.

5. Further Information and Synthesis of Part 2

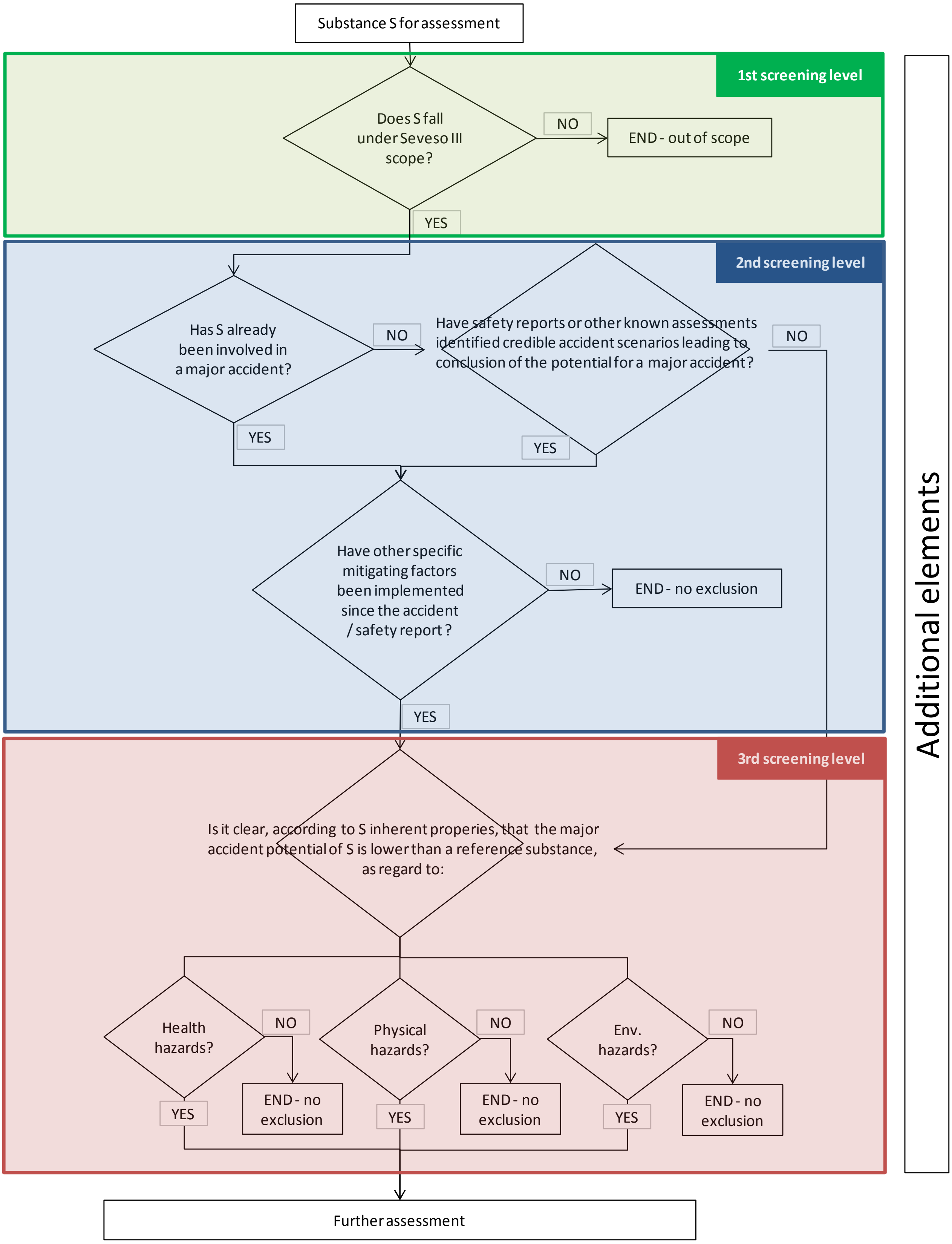
After the initial screening, the member states should document the reasoning as to whether further analysis is warranted or if it is already clear that a potential for major accident hazard exists. A further option for the initial screening would be to take the available data on the substance and information on its conditions of use (e.g. as referred to in Step 3 above), to answer a number of preliminary questions as to why the substance might be relevant for exclusion under Article 4. The idea at this stage would not be to come to a definitive conclusion, but to clearly set out a reasoned argument that Article 4 might be relevant. Such steps could be based on the points in Article 4(1) and 4(3) and could include:

- Reviewing whether the physical form in use and under ambient conditions (based on physicochemical properties) suggest that the substance cannot disperse widely following an accidental release or a fire/explosion.
- Reviewing whether other physicochemical properties preclude widespread dispersion of the substance (e.g. vapour pressure), for example in comparison to other substances listed on Annex I.
- Reviewing whether an exclusion from the scope of Seveso III might only be relevant for mixtures with a certain maximum concentration of the substance. (For example a substance with a concentration high enough for the mixture to be included under Annex I part 1, but not high enough for the relevant toxic effects to occur in practice e.g. for fuming versus more dilute acids).
- Checking whether there is specific containment or packaging that is always applied (e.g. where required by EU law) which would prevent the release of the substance in large quantities, or prevent a fire or explosion involving the substance. This is considered in Step 2 above, but the outcomes of Step 3 (which follows on from Step 2) might not allow a definitive conclusion to be reached.

The idea here is not to conclude definitively whether the substance has potential for major accident hazard (or not), but to act as an additional check to see whether there are any overriding factors that mean further assessment is warranted (i.e. which might not have been picked up by the preceding steps). This approach would enable one to draw upon expert judgement to describe whether a substance seems like a credible candidate to take forward to more detailed analysis. If no credible argument can be made based on readily available information (without the need for detailed analysis), it is likely that the substance will have potential for major accident hazard if realistic worst-case (foreseeable) conditions across the EU are taken into account.

The flowchart below (Figure 5.1) synthesises the three steps envisaged for the initial screening stage.

Figure 5.1 Flowchart of the initial screening steps



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Appendix A
Exclusions from scope under Article 4 of Seveso III and dispensations under Article 9 of Seveso II

This appendix provides a summary of the description of where exclusions under Article 4 of Seveso III may occur and the dispensations under Article 9(6) of Seveso II, as there are some parallels in the information used to justify exemption under the two Articles. However, while the descriptors used in the two approaches are in some cases similar, there is a fundamental difference in that Seveso II Article 9(6) dispensations are relevant for individual establishments, while Seveso III exemptions from scope under Article 4 need to take into account EU-wide applicability of the decision criteria.

Exclusions from scope of Seveso III

The text of Article 4 of the Seveso III Directive is as follows:

> *1. The Commission shall assess, where appropriate or in any event on the basis of a notification by a Member State in accordance with paragraph 2, whether it is impossible in practice for a particular dangerous substance covered by Part 1 or listed in Part 2 of Annex I, to cause a release of matter or energy that could create a major accident under both normal and abnormal conditions which can reasonably be foreseen. That assessment shall take into account the information referred to in paragraph 3, and shall be based on one or more of the following characteristics:*
>
> *(a) the physical form of the dangerous substance under normal processing or handling conditions or in an unplanned loss of containment;*
>
> *(b) the inherent properties of the dangerous substance, in particular those related to dispersive behaviour in a major- accident scenario, such as molecular mass and saturated vapour pressure;*
>
> *(c) the maximum concentration of the substances in the case of mixtures.*
>
> *For the purposes of the first subparagraph, the containment and generic packing of the dangerous substance should, where appropriate, also be taken into account, including in particular where covered under specific Union legislation.*
>
> *2. Where a Member State considers that a dangerous substance does not present a major-accident hazard in accordance with paragraph 1, it shall notify the Commission together with supporting justification, including the information referred to in paragraph 3.*
>
> *3. For the purposes of paragraphs 1 and 2, information necessary for assessing the health, physical and environmental hazard properties of the dangerous substance concerned shall include:*

(a) a comprehensive list of properties necessary to assess the dangerous substance's potential for causing physical, health or environmental harm;

(b) physical and chemical properties (for instance molecular mass, saturated vapour pressure, inherent toxicity, boiling point, reactivity, viscosity, solubility and other relevant properties);

(c) health and physical hazard properties (for instance reactivity, flammability, toxicity together with additional factors such as mode of attack on the body, injury to fatality ratio, and long-term effects, and other properties as relevant);

(d) environmental hazard properties (for instance ecotoxicity, persistence, bio-accumulation, potential for long-range environmental transport, and other properties as relevant);

(e) where available, the Union classification of the substance or mixture;

(f) information about substance-specific operating conditions (for instance temperature, pressure and other conditions as relevant) under which the dangerous substance is stored, used and/or may be present in the event of foreseeable abnormal operations or an accident such as fire.

4. Following the assessment referred to in paragraph 1, the Commission shall, if appropriate, present a legislative proposal to the European Parliament and to the Council to exclude the dangerous substance concerned from the scope of this Directive.

Scope of dispensations under Article 9 of Seveso II

Article 9 of the Seveso II Directive requires that the operators of upper tier establishments produce and periodically review a safety report and send it for examination to the national competent authority. Article 9(6) provides for possible dispensations on the information contained in safety reports to be granted by the competent authorities of the Member States, upon request from operators of upper tier establishments, as follows:

6. (a) Where it is demonstrated to the satisfaction of the competent authority that particular substances present at the establishment, or any part thereof, are in a state incapable of creating a major-accident hazard, then the Member State may, in accordance with the criteria referred to in subparagraph (b), limit the information required in safety reports to those matters which are relevant to the prevention of residual major-accident hazards and the limitation of their consequences for man and the environment.

(b) The Commission shall establish harmonised criteria for decisions of the competent authority that an establishment is in a state incapable of creating a major accident hazard within the meaning of subparagraph (a). Those measures, designed to amend non-essential elements of this Directive by supplementing it, shall be adopted in accordance with the regulatory procedure with scrutiny referred to in Article 22(3).

(c) Member States shall ensure that the competent authority communicates a list of the establishments concerned to the Commission, giving reasons. The Commission shall forward the lists annually to the Committee referred to in Article 22.

A Technical Working Group was organised in order to prepare the harmonised criteria. Those criteria are described in the document called “Explanations and Guidelines” and established by the Commission in its Decision 98/433/EC.

Table A1 Harmonised criteria for application of Article 9 of Seveso II

Harmonised criteria	Details about criteria	Explanation taken from the document “Explanations and Guidelines”
1. Physical form of substance	Substances in solid form, such that, under both normal conditions and any abnormal conditions which can reasonably be foreseen, a release, of matter or of energy, which could create a major-accident hazard, is not possible.	The fact that the physical form of certain substances influences their major-accident potential is recognised in the Seveso II Directive. For example, the entry for nickel compounds only in inhalable powder form in the list of named substances in Annex I, Part 1 of the Directive reflects the fact that these compounds when in solid form are incapable of creating a major-accident hazard, despite their being classified as being toxic.
2. Containment and quantities	Substances packaged or contained in such a fashion and in such quantities that the maximum release possible under any circumstances cannot create a major-accident hazard.	This criterion can only be applied if the quantities taken out of containment at any one time are insufficient to create a major-accident hazard. This criterion could be applied to a store of containers of such size, construction, and contents that the release from a small number of containers would not in itself represent a major-accident hazard nor could it have any knock-on effects on other containers, provided that no reasonably foreseeable external aggression could release the contents of a large number of containers.
3. Location and quantities	Substances present in such quantities and at such distances from other dangerous substances (at the establishment or elsewhere) that they can neither create a major-accident hazard by themselves nor initiate a major accident involving other dangerous substances.	A large establishment consisting of several installations may have dangerous substances in small and isolated quantities at installations distant from those which represent the major-accident hazard potential, and also from any other hazardous establishments. The inability to cause a major accident, directly or indirectly, must apply to the substances concerned at all moments that they are present at the establishment. It should also be borne in mind that substances will have to be transported within the establishment, and during transport this criterion may not apply.
4. Classification	Substances which are defined as dangerous substances by virtue of their generic classification in Annex I, Part 2 to Directive 96/82/EC, but which cannot create a major-accident hazard, and for which therefore the generic classification is inappropriate for this purpose.	Since the generic classifications of Annex I, Part 2 are based on the intrinsic hazard associated with a substance, there may be cases where this is not relevant in the context of a major accident. This criterion could apply to a substance which is classified as toxic, but for which the only hazard is toxicity by ingestion, provided that route of exposure can reasonably be excluded in the event of a major accident. This criterion cannot apply to substances which are listed in Annex I, Part 1.

These criteria were expected to have been applied to the individual notifications of dispensations (these are site specific site-specific). However, unlike Seveso III Article 4, there was no process for review of notifications under Seveso II Article 9(6)

A number of dispensations have been granted by European competent authorities, as shown in the table below.

Table A2 List of the dispensations in the context of Article 9(6) of Seveso II Directive

EU Country	Name of the substance	Details for the derogation request (elements taken from official requests)
UK	Nickel compounds in inhalable powder form (nickel oxide)	Nickel compounds in inhalable powder form is a named substance in Seveso annex 1 part 2. The argument for granting the dispensation is that all the toxicological evidence indicates that there is no risk from single shot exposure.
Belgium	Amino Functional Fluid Conditioning Agent (very toxic by ingestion)	The substance is not pressurised and it is impossible to form a hazardous aerosol that could create a major accident
Italy	Mixture of sodium (60%) nitrate and potassium nitrate (40%)	The nature of the containment, the location of the storage and quantities explained that no major accident is forecasted.
Luxembourg	Nickel-based compounds used as catalysts	The derogation is based on the nature of the containment and the quantity stored.
Germany	Ammonia Lithium chloride Lithium bromide Sulphur dioxide Acetylene Propane Cryogenic Liquefied oxygen	

In the table below, the criteria based on Article 9(6) of the Seveso II Directive are “challenged” with respect to their applicability in the context of Article 4 of the Seveso III Directive.

Table A3 Commentary on Seveso II Article 9(6) criteria and relevance for Article 4 of Seveso III

Harmonised criteria	Details about criteria	Relevance in the assessment methodology under Article 4 of Seveso III?
1. Physical form of substance	Substances in solid form, such that, under both normal conditions and any abnormal conditions which can reasonably be foreseen, a release, of matter or of energy, which could create a major-accident hazard, is not possible.	Physical form of substance is considered in the Initial screening (see Task 1), whose objective is to eliminate substances which clearly have the potential to generate a major accident. It is also considered in determining whether there are relevant accident scenarios. This is an important criterion in the context of Article 4.

Harmonised criteria	Details about criteria	Relevance in the assessment methodology under Article 4 of Seveso III?
2. Containment and quantities	Substances packaged or contained in such a fashion and in such quantities that the maximum release possible under any circumstances cannot create a major-accident hazard.	Containment and quantities are considered in the definition of worst case scenarios (see Tasks 4 and 5). However, it is much easier to justify an exclusion under Article 9(6) which applies at an individual site level, compared to Article 4 of Seveso III where the exemption would need to apply at EU level.
3. Location and quantities	Substances present in such quantities and at such distances from other dangerous substances (at the establishment or elsewhere) that they can neither create a major-accident hazard by themselves nor initiate a major accident involving other dangerous substances.	The question of location is not valid in the context of Article 4 because Article 4 of Seveso III is to be applied to EU wide exemptions. However, the criterion “quantities” is taken into account in the definition of the worst case scenarios.
4. Classification	Substances which are defined as dangerous substances by virtue of their generic classification in Annex I, Part 2 to Directive 96/82/EC, but which cannot create a major-accident hazard, and for which therefore the generic classification is inappropriate for this purpose.	The criteria “classification” is consider in the initial screening.

Appendix A
Exclusions from scope under Article 4 of Seveso III and dispensations under Article 9 of Seveso II

This appendix provides a summary of the description of where exclusions under Article 4 of Seveso III may occur and the dispensations under Article 9(6) of Seveso II, as there are some parallels in the information used to justify exemption under the two Articles. However, while the descriptors used in the two approaches are in some cases similar, there is a fundamental difference in that Seveso II Article 9(6) dispensations are relevant for individual establishments, while Seveso III exemptions from scope under Article 4 need to take into account EU-wide applicability of the decision criteria.

Exclusions from scope of Seveso III

The text of Article 4 of the Seveso III Directive is as follows:

> *1. The Commission shall assess, where appropriate or in any event on the basis of a notification by a Member State in accordance with paragraph 2, whether it is impossible in practice for a particular dangerous substance covered by Part 1 or listed in Part 2 of Annex I, to cause a release of matter or energy that could create a major accident under both normal and abnormal conditions which can reasonably be foreseen. That assessment shall take into account the information referred to in paragraph 3, and shall be based on one or more of the following characteristics:*
>
> *(a) the physical form of the dangerous substance under normal processing or handling conditions or in an unplanned loss of containment;*
>
> *(b) the inherent properties of the dangerous substance, in particular those related to dispersive behaviour in a major- accident scenario, such as molecular mass and saturated vapour pressure;*
>
> *(c) the maximum concentration of the substances in the case of mixtures.*
>
> *For the purposes of the first subparagraph, the containment and generic packing of the dangerous substance should, where appropriate, also be taken into account, including in particular where covered under specific Union legislation.*
>
> *2. Where a Member State considers that a dangerous substance does not present a major-accident hazard in accordance with paragraph 1, it shall notify the Commission together with supporting justification, including the information referred to in paragraph 3.*
>
> *3. For the purposes of paragraphs 1 and 2, information necessary for assessing the health, physical and environmental hazard properties of the dangerous substance concerned shall include:*

> *(a) a comprehensive list of properties necessary to assess the dangerous substance's potential for causing physical, health or environmental harm;*
>
> *(b) physical and chemical properties (for instance molecular mass, saturated vapour pressure, inherent toxicity, boiling point, reactivity, viscosity, solubility and other relevant properties);*
>
> *(c) health and physical hazard properties (for instance reactivity, flammability, toxicity together with additional factors such as mode of attack on the body, injury to fatality ratio, and long-term effects, and other properties as relevant);*
>
> *(d) environmental hazard properties (for instance ecotoxicity, persistence, bio-accumulation, potential for long-range environmental transport, and other properties as relevant);*
>
> *(e) where available, the Union classification of the substance or mixture;*
>
> *(f) information about substance-specific operating conditions (for instance temperature, pressure and other conditions as relevant) under which the dangerous substance is stored, used and/or may be present in the event of foreseeable abnormal operations or an accident such as fire.*
>
> *4. Following the assessment referred to in paragraph 1, the Commission shall, if appropriate, present a legislative proposal to the European Parliament and to the Council to exclude the dangerous substance concerned from the scope of this Directive.*

Scope of dispensations under Article 9 of Seveso II

Article 9 of the Seveso II Directive requires that the operators of upper tier establishments produce and periodically review a safety report and send it for examination to the national competent authority. Article 9(6) provides for possible dispensations on the information contained in safety reports to be granted by the competent authorities of the Member States, upon request from operators of upper tier establishments, as follows:

> *6. (a) Where it is demonstrated to the satisfaction of the competent authority that particular substances present at the establishment, or any part thereof, are in a state incapable of creating a major-accident hazard, then the Member State may, in accordance with the criteria referred to in subparagraph (b), limit the information required in safety reports to those matters which are relevant to the prevention of residual major-accident hazards and the limitation of their consequences for man and the environment.*
>
> *(b) The Commission shall establish harmonised criteria for decisions of the competent authority that an establishment is in a state incapable of creating a major accident hazard within the meaning of subparagraph (a). Those measures, designed to amend non-essential elements of this Directive by supplementing it, shall be adopted in accordance with the regulatory procedure with scrutiny referred to in Article 22(3).*

> *(c) Member States shall ensure that the competent authority communicates a list of the establishments concerned to the Commission, giving reasons. The Commission shall forward the lists annually to the Committee referred to in Article 22.*

A Technical Working Group was organised in order to prepare the harmonised criteria. Those criteria are described in the document called "Explanations and Guidelines" and established by the Commission in its Decision 98/433/EC.

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