

## Foreword

Introduction of the EU Directive 96/82/EG “Seveso II” as regards location supervision according to section 12, requires that so-called reference scenarios and thus derived safety margins are established for regional development and area planning purposes, which can also be used as a basis for emergency plans according to section 11.

The systematic search for potential dangers, the selection of accident scenarios and especially the necessary assessment of the extent of damage and severity of consequences, often lead to extreme difficulties due to the lack of expert knowledge and suitable propagation models for computation purposes.

It is thus the objective of this study to furnish the competent authorities, on the basis of examples and demonstrations, with a tool for the assessment of the necessary safety margins and the severity of accident consequences. It is also intended to provide information on the potential environmental danger that stems from the dealing with chemicals.

It is further intended to provide this tool for the largest circle of users possible. Certain basic technical knowledge is presupposed, primarily in the use of tables and diagrams for solving technical problems.

The simplified description and assessment of complex processes, due to the extensive applicability of the tool, provides a large area for criticism. This guideline is thus primarily intended for a quick assessment of possible accident results and safety margins. Scenarios and assumptions of possible releases of substances should be defined or made in direct co-operation with the operators of the respective plant. The final safety margins should then be established on the basis of plant-specific calculations.

The study is based partly on the practical experience of the author with accident scenarios and impact calculations within the framework of safety analyses, and partly on valuable suggestions from the Swiss publication (Koordinationsstelle für Störfallvorsorge Zürich) on “Schadenausmaß-Einschätzung” (accident impact assessment) and further on course documents “hazard analysis course notes” of ICI Australia and on the study “Voruntersuchungen zur Anwendung eines Schwergasmodells bei Industrieunfällen” (preliminary analyses on the use of a heavy gas model in industrial accidents) from the Central Institute for Meteorology and Geodynamics, Vienna, Austria.

This paper should not be considered as completed. There are still uncertainties, especially in the propagation model for heavy toxic gases, as shown and discussed in chapter 13.4. New facts or recommendations from a current European evaluation will, when available, be incorporated.

Vienna, Austria, July 1999.

## **1. INTRODUCTION**

In a meeting on “The Seveso II Directive and its effect on Austria” in Linz, Austria on April 28, 1996, organised by Austrian Plant Safety Forum, it was pointed out among other things, that technical novelties are expected in this field and that “reference scenarios” or probabilistic approaches in risk and danger assessment will have to be looked at more closely.

For better understanding of the background of safety philosophy, some terms which are frequently used in the discussions are explained here and related in the current context.

### **1.1 Integral approach to safety and environmental protection**

Dealing with high technological danger potentials in process plants requires a prevention concept by which the impacts from potential dangers can be avoided by socially acceptable measures. The EU Seveso I and Seveso II Directives play a central role. These Directives develop a hierarchical multi-step safety concept and define it for the area of chemical process engineering.

In order to comply with the basic safety principles of these Directives, an integrated safety concept was worked out for potentially dangerous industrial plants. The basic structure is a hierarchic three-step system which may be characterised by:

step 1, all measures in a plant that bar the entrance of hazardous substances and/or the development of inadmissible operating conditions,

step 2, all plant-related measures which help minimise accident-caused impacts (release, fire, explosion), and

step 3, all measures for the lowering of accident impacts from danger sources in the vicinity (exposure to pollutants, heat radiation, pressure waves, debris).

The logic of the system sees objects of protection becoming exposed to danger (by sources in the neighbourhood, the environment) only if all three safety steps fail to function simultaneously. With the measures in the individual steps being independent of those in the other steps, such simultaneous failure is highly improbable, especially since the measures of step one and two are plant-related and those of step three environment-related.

Such an integrated safety system requires systematic safety examinations to be carried out in form of safety analyses.

This three-step safety concept has been realised within the framework of the Austrian Accident Regulation.

### **1.2 Analysis of consequences of possible severe accidents**

The three-fold examination of accident-caused consequences required by the Seveso II Directive, in section 9 of the Safety Report, in section 11 of the Emergency Plans and in section 12 on Inspection of Locations, appear to be contradictory at first sight.

On the one hand, the Safety Report stipulates detailed safety measures, and on the other, still larger accidents causing release, fire or explosion shall be assumed and possible consequences shall be stated.

This apparent contradiction is resolved when the purpose of the Directive is considered more closely.

Two levels are here to be distinguished:

Level 1:

The analysis of accident consequences at level 1 shall be regarded as a means by which the efficiency of the measures taken, especially those for limiting the consequences, can be verified. This analysis shall thus be based on situations which have repeatedly led to severe accidents in practice, e.g. release due to a ruptured hose during charging or discharging, damaged seals or fittings, corroded piping, etc. Constant registration of severe accidents is here of importance. From the analyses of consequences, clues shall then be derived and used to plan effective in-plant danger countermeasures.

Level 2:

The analysis of the accident consequences at level 2, which designed to provide information useful for planning protective measures against external danger, starts out from different premises. The data or more precisely, the data of accident consequences, are based on the assumption that a “severe accident” with serious danger to humans and the environment, as dealt with in the Seveso II Directive, has already happened. Such an accident is a source of the serious danger. With quantity thresholds being characteristic values which refer to the whole plant set-up, the restriction to the maximum interconnected quantity of substance in the plant can be regarded as a realistic approach. Scenarios for emergency plans and for the supervision of industrial settlements, according to section 11 and 12 of Seveso Directive II belong to this level.

While accidents of level 1 occur with a high degree of probability but can be avoided by appropriate technical and organisational measures, it is not possible to prevent a “hypothetical incident” or severe accident of level 2 despite the practically negligible probability of occurrence. This is to say that “hypothetical incidents” require no consideration of (active) accident-prevention measures. Among German-speaking experts, this “hypothetical incident” is sometimes also referred to as “exceptional incident”. The term “worst case”, often used in the German and English literature, is generally applied for accidents (from a spectrum of various scenarios) with the worst consequences, i.e. accidents of level 2. In order to limit the consequences of such possible severe accidents, an emergency plan for the prevention of danger from outside is required. Such measures can help reduce consequences of accidents, but can never avoid accidents.

### **1.3 Reference scenario method; deterministic approach**

In order not to overshoot the mark when selecting scenarios of possible severe accidents, the “reference scenarios” method was developed, which is extensively used in France. The scenarios are defined on the basis of practical experience and predominantly in terms of records of severe accidents in specific types of plant.

In order to obtain a plant operating licence, the operator has to prove that measures are in place which will minimise the possible risks or consequences specified in the respective reference scenarios. The result are safety margins which can be used as a basis for decision and planning in area planning.

The “Maximum Credible Accident”, the MCA, was introduced as a principle for safety engineering decisions in reactor technology already between 1955 and 1960. It represents the worst accident with consequences that can be controlled by plant-specific protection measures. Between 1965 and 1970, the safety engineering principle of “layout accidents” was introduced and a large spectrum of possible accident scenarios was considered in the plant layouts. The approach is called “deterministic”.

#### **1.4 Probabilistic approach**

A second method, preferred by some of the EU member states, is the “probabilistic” approach.

While the deterministic method (consequence-oriented) produces, on the basis of reference scenarios, zones of lethality and severe injuries, the probabilistic method (risk-oriented) yields zones in which a specified extent of damage (risk criterion), as result of all possible accidents with calculated probabilities is to be expected.

For a clearer understanding of these two approaches in safety engineering, here are some additional explanations.

#### **1.5 Deterministic/probabilistic approach**

The ever increasing complexity of technical systems and the higher safety engineering and economic requirements to be fulfilled by them, especially in area utilisation planning of densely populated areas, have made quantitative safety parameters increasingly important, but not replaced the proven deterministic approach.

Probabilistic methods are nowadays primarily used for checking the balance of safety concepts. Moreover, they are used as a tool in decision-making processes

- for plant layout optimisation,
- for the evaluation and valuation of operational practice,
- for detailed description of achieved safety levels,
- for the valuation of the course of incidents which extend beyond the plant layout (deterministic approach),
- for the planning of maintenance and repair strategies and
- for the setting of priorities in safety research.

The use for reliability and risk analyses has become standard practice, primarily in space travel, shipbuilding, reactor engineering and in many fields of process and energy engineering and it is also applied for traffic systems.

As already mentioned, probabilistic methods are essentially used in checking the balance of applied safety programmes. They are further applied as a complementary tool for safety analyses in safety equipment layouts for danger-prone plants.

It is the basis for the preparation of risk studies and will be used ever more in the future. It could also become an important instrument in decisions concerning necessary modernisation of danger-prone plants.

From an EU Commission report on “Land Use Planning in the Context of Major Accident Hazards, an Analysis of Procedures and Criteria in Selected EU Member States” of 1996, it can be derived that area utilisation planning in densely populated areas in countries such as Belgium, Denmark, The Netherlands and the UK, is based on the so-called “risk-oriented” probabilistic method. In Belgium (using the other also), Finland, France, Germany, Luxembourg, Spain and Sweden, the so-called “consequence-oriented” deterministic method is used. In France, Germany, Luxembourg, the Netherlands and the UK, other criteria (e.g. risk criteria) are also in use in area utilisation planning. At present, Austria and many other EU member countries have not finally settled on a specific method.

In Austria, granting of plant operation licences had never been based on probabilistic methods, the approach was always purely deterministic. This fits in with the current safety philosophy and also with the structure of the safety analyses. Since probabilistic methods are unstoppable on the advance, Austria should provide the necessary prerequisites as quickly as possible. This means, among other things, continuous registration of severe accidents and setting up of a data base for failure data of plant components and systems in process plants.

For proper understanding of probabilistic safety analyses (PSA), sometimes also referred to as PRA (“probabilistic risk assessment”) or QRA (“quantified risk assessment”), it should be remembered, for example, that layouts of (danger-prone) process plants, just as in other fields of engineering, still have a deterministic starting platform that consists of applicable functions, engineering rules, experience and other fundamentals. The decision on the quality standard is deterministic and so is the decision whether a plant should be furnished with an accident-avoiding or a damage-restricting system or, for example, be provided with a double lock in a pipe line.

In order objectively to compare the probabilistic approach with the deterministic, both approaches will be demonstrated by an example of a bridge layout (see Figure 1).

At the start, the bridge is deterministically laid out for a load-bearing capacity clearly above its loading, as shown in the upper part of Figure 1.

With a probabilistic approach for the layout, it must in principle be assumed that the effective load and also the load transfer, as shown in the lower part of Figure 1, are allowed to deviate, with the magnitude and probability of the deviations being inversely proportional. In the worst case, the most improbable case, the operating load, e.g. due to simultaneous loading by storm, snow and soldiers marching in step, is excessively high and the load bearing capacity of the bridge, due to a coincidence of faulty material, erosion and corrosion, is excessively low, so that the area of overlap (lower part of Figure 1) is reached and the bridge is bound to break. With PSA, both probability graphs must be quantified and the residual risk calculated.

For a proper introduction of PSA, we should add something about its history. More than twenty years ago (before 1970), efforts were made to improve the reliability of systems of utmost importance, e.g. in shipbuilding and space travel, via probabilistic checks.

The Rasmussen study of 1975 was the first comprehensive risk examination of a technological plant and a comparison with other risks of civilisation and nature. This analysis and the “Deutsche Risikostudie Phase A” (the German Risk Study) on the nuclear power station Biblis B then led to a broad recognition and to discussions on probabilistic analyses, particularly among experts.

Viewing the overall development also requires looking at the current international situation and the use of PSA in other technical fields. In practically all Western countries individual PSA became standard for weak-spot analyses, primarily in the field of nuclear power.

In fields outside nuclear power, there have been multiple endeavours towards the use of probabilistic methods in improving the availability and safety of complex systems and in assessing the implications of risks in the chemical industry (Lyon Project in France, Canvey Island Project in UK, Rijnmond Project in the Netherlands, ARIPAR and ARTIS projects in Italy).

The Seveso II Directive reflects the potential of modern reliability technology in the whole field of process industry subject to this Directive. From experience in nuclear power, the whole field of process engineering was recommended by the authority to have its risk assessments based on risk models. This means that a possible loss caused by a barring of a certain technology, after definition and presentation of its inherent risks, may prove to be of less consequence than the gain achieved from the avoidance of the risks uncovered by the analyses.

It should further be mentioned that the use of deterministic schemes in physics leads essentially to differential equations which express determination, e.g. force is the product of mass and acceleration, in other words, represent a law of nature.

In statistical mechanics, which was developed from thermodynamics, probability has become the central concept. It is remarkable that without knowing the initial parameters of the involved particles and without calculation of their paths, deterministic (basic natural) laws were able to be derived, e.g. the ideal gas law.

It is understandable that decades ago when complex processes had to be calculated with slide rules and the most simple mechanical calculators and measuring instruments, interrelationships were presented most rigorously simplified. Variables with their parameter uncertainties were made fixed quantities and random variables (especially the so-called rare events) were neglected. Perfect functioning of man and machine was assumed. High capacity calculators and increased knowledge in conceptual modelling and of real operational behaviour of all kinds of process plant permit solving complex issues by complex analyses via suitable models.

### **1.5.1 Completeness of analyses**

Erection and operation of process plants, as already mentioned, are predominantly deterministically governed. Determining means deciding, as result of extensive examination, that a certain course of events cannot possibly occur.

Countermeasures are thus not required. Other events, however, cannot be excluded and countermeasures must thus be provided. Each particular event will be allocated, on the basis of knowledge, a probability factor of occurrence from zero to one.

The question of completeness of the spectrum of considered events is solved by treating only the most representative of combined similar events.

In probabilistic analyses the occurrence of events and also the presence of measures for the control of these events is considered with a random probability between 0 and 1. The experience available for either qualitatively deciding on “neglecting or considering a certain event” or for quantitatively determining of probabilities, is of course the same.

But since PSA, contrary to a deterministic method, produces quantitative results, the question on possible contributions by unconsidered events weighs heavier. This is to say that PSA relies on a full spectrum of events being considered and on quantitative probability criteria. The spectrum of events considered comprises not only physically observable events but also hypothetical ones. It can thus be derived that e.g. in nuclear power, events which occur with a probability lower than  $10^{-7}$  per year do not need to be analysed. The general conclusion is that, in accordance with the latest developments in research and with state-of-the-art technology, the respective spectrum of initiating events has to be as complete as possible.

## **2. ACCIDENT SCENARIOS**

### **2.1 Aim**

According to chapters 11 and 12 of the Seveso II Directive, it is required that the extent of damage from severe accidents as regards possible damage to the population and the environment has to be assessed either deterministically or probabilistically or by a method using both principles.

This study serves to support the authorities in drawing up accident scenarios and assessing the dimensions of the consequences. A series of examples which shall serve as a basis, can be modified with the help of the enclosed tables to suit specific local conditions.

For general applicability, certain simplifications as to the (complete) course of the most unfavourable event (e.g. initial phase/release) had to be made. Calculations of propagation and of impacts were made with pessimistic assumptions, restricted to reference substances, and the impact distances were assessed with reference to the most unfavourable single event, i.e. release, fire or explosion. Combined events must be treated correspondingly.

Simplifications and restrictions are listed for each scenario. As already mentioned, “hypothetical incidents” exclude consideration of (active) accident-avoiding measures (section 3).

The various phases in the assessment of the extent of damage are schematically presented in the following:

## 2.2 Sequence of assessment of accident consequences

The general procedure in the consequence analysis after a severe accident is as follows:

Phase	Criteria	Tool
Initiating event ↓	Release Fire Explosion	
Danger characteristics ↓	Relevant physical and chemical properties Hazard classification	Safety data sheet Supplier Literature
Propagation path ↓	Ground Water Air	
Influence distance ↓	State of aggregation Form of release Quantity of substance (*) Weather/wind	Tables in guideline
Surroundings ↓	Topography Density of settlement Sensitive buildings	Maps Land registry plan
Assessment of consequences	People Ecosphere Infrastructure	Superposition of accident zones and settlement density

(\*)With quantity thresholds in the Seveso II Directive being parameters related to the whole plant set-up, the restriction to the maximum interconnected volume of substance within the plant is a realistic approach.

## 2.3 Possible accident scenarios

On the basis of the dangerous properties of a substance, accident scenarios can be categorised as to their consequences:

### 2.3.1 Release of liquids and solid matter (leakage)

Contamination of soil and of ground and surface water, killing of aquatic life, damage to public supply and disposal facilities such as drinking water reservoirs and sewage plants.

Involved substances: Substances of relevant water pollution categories, e.g.

Mineral oil

- Inorganic acids and liquors
- Chlorinated hydrocarbons
- Organic solvents
- Heavy metals
- Cyanides



### **2.3.2 Release of gases**

Such release can cause toxication of people and animals through large-scale propagation of heavy toxic gases. Danger to very sensitive public institutions such as schools, hospitals, old people's homes, supermarkets (restricted possibilities for escape, rather problematic evacuation)

Involved substances: Toxic gases, e.g.

Chlorine  
Ammonia  
Hydrogen chloride  
Hydrogen cyanide

and other combinations of substances which, when permitted to combine, release highly toxic gases, e.g.:

Hydrochloric acid and Javelle water = potassium hypochlorite (chlorine)  
Hydrochloric acid and sodium chlorite (sodium chloride)  
Cyanide-containing salts and acids (hydrogen cyanide)

### **2.3.3 Fire/explosion**

Immediate effects on population and buildings from an explosion or intensive fire with after-effect from projected or falling debris, pressure wave and heat radiation.

Involved substances: Easily inflammable or inflammable liquids and combustible gases, e.g.

Organic solvents  
Benzine, gasoline, naphtha  
Liquid gas (propane, butane)

### **2.3.4 Selection of accident scenarios**

Of foremost importance in the selection of the accident scenarios are the most dangerous properties (physical and chemical substance parameters) and the state of aggregate of the substances involved in the accident. This leads automatically to the scenarios to be considered which must be complemented with data concerning the individual local conditions and the surroundings. Accident scenarios can thus be presented as shown:

### Accident scenarios: Toxic/ecotoxic substances

Danger potential	Toxic or ecotoxic substances ⇓	
Accident	Leakage (pressurised/non-pressurised) ⇓	
State of aggregate	liquid (direct input) ⇓	gaseous (airborne substances) ⇓
Consequences	Toxication Pollution - surface waters - groundwater - soil contamination	Gas cloud without fire - heavy toxic gases - e.g. ammonia, chlorine
Treated in	chapter 12	chapter 13

### Accident scenarios: Combustible or explosive substances - Accident: Fire

Danger potential	Combustible or explosive substances		
Accident	Fire ⇓		
State of aggregate	solid ⇓	liquid ⇓	liquid/gaseous ⇓
Consequences	solids on fire dust explosion	pool fire tank fire	fire ball “BLEVE” boil over jet fire
treated in	chapter 9	chapter 7	

Pool fire: Burning collecting basin; surface fire

Tank fire: Burning tank

Boil over: Fire ball caused by a boil over (of a burst container or roof-covered tank with combustible liquid exposed to heat or flames)

“BLEVE”: Boiling Liquid Expanding Vapour Explosion (burst container with pressure-liquefied combustible gas exposed to heat or flames)

Jet fire: Open jet fire (burning immediately at discharge opening)

Flash fire: Rapid combustion of a gas cloud without creation of a pressure wave

**Accident scenarios: Combustible or explosive substances - Accident: Explosion**

Danger potential	Combustible or explosive substances ↓		
Accident	Explosion ↓		
State of aggregate	solid ↓	liquid ↓	gaseous ↓
Consequences	Explosive decomposition Reactive substances Blasting agents e.g. T.N.T.	Explosive decomposition reactive substances	Gas cloud explosion UVCA/VCE
treated in	chapter 11	chapter 11	chapter 10

UVCE: Untamped Vapour Cloud Explosion

VCE: Tamped Vapour Cloud Explosion

**2.3.5 Severe accidents in danger-prone plants**

The following types of severe accidents can theoretically happen in danger-prone process industries:

- A. Fire
- B. Flash fire
- C. UVCE/VCE
- D. Fire ball/BLEVE/boil over
- E. Dust explosion
- F. Other forms of explosion
- G. Release of toxic gases
- H. Toxic fire gases

**An overview broken down by substances and relevant plants:**

Substances/Plants and facilities	Possible accidents
Liquefied combustible gases	
Pressurised storage	A,B,C,D
Storage under atmospheric pressure	A,C,D
Process plant	A,B,C,D
Tank wagon/truck filling and draining	A,B,C,D
Road/railroad transport	A,B,C,D
Ship and shipyard operation	A,B,C,D
Long distance pipelines	A,C,D
Combustible liquids	
Tank storage	A
Barrel storage	A,B
Process plant	A,B,C,D
Tank wagon/truck filling and draining	A
Road/railroad transport	A
Ship and shipyard operation	A
Long distance pipelines	A
Combustible gases	
Storage or production	A,C,D
Combustible dusts (or dust-creating solids)	
Storage or production	A,E
High-reaction substances	
Storage	A,D,E,F,H
Production	A,D,E.F.H
Toxic gases	
Storage	G
Processing, production	G
Substances with toxic combustion products	
Storage or processing	H

### 3. CONSIDERATION OF SAFETY MEASURES AND FACILITIES

For the assessment of possible consequences after an accident, the principal approach is to start at a possible failure of the primary enclosure (packing, barrel, tank, container, reactor, piping). The extent of the damage is essentially determined by the type and quantity of substances involved, the course of the accident and a (possible) presence of retainers or barriers.

Barriers in a water-polluting accident are, for example:

- Collecting basins
- Fire-fighting water retaining basins
- Prepared cellars

Barriers in an accident with fire are, for example:

- Fire protection building measures
- Shield walls ( against heat radiation)
- Soil covers (no undergrate firing)

Passive safety measures such as a fire protection building measures (fire-proof compartments), concrete collecting basins, fire fighting water retaining basins or soil covers may generally, for safety considerations, be regarded as limiting or barring measures. If the possibility of explosions cannot be excluded, protective building measures may nevertheless turn out to be insufficient.

As already mentioned, “hypothetical incidents” categorically exclude a sensible use of preventive measures, i.e. active safety measures such as MSR facilities, alarm systems and fire-controlled safety functions, since their reliability can, in principle, not be guaranteed. The same is true for intervention programmes based on alarm and counteraction plans.

#### **4. ACCIDENT SCENARIOS – DECISIVE PARAMETERS AND FACTORS OF INFLUENCE**

The general approach to analysing the consequences of severe accidents has already been presented in chapter 2.2. The selection of important accident scenarios is oriented rather on the extent of possible damage to the population and the environment than on the probability of occurrence. However, there is no good reason to exclude a scenario with a very low probability from the list of essential scenarios.

When examining important accident scenarios, three questions need to be answered:

Mechanisms of release → effect of release → consequences of a release for the population and the environment.

Decisive parameters and factors of influence for accident scenarios:

	<b>Decisive parameters</b>	<b>Factors of influence</b>
<b>Release</b>	<p>kind and magnitude of leakage</p> <p>volume and rate of leakage</p> <p>size of the pool</p> <p>rate of evaporation</p>	<p>cause of leakage</p> <p>state of aggregate of released substance gaseous liquid two-phase</p> <p>full quantity released minus portion evaporated or turned into aerosols characteristics of the soil</p> <p>evaporation mechanism</p>
<b>Effect</b>	<p>concentration of pollutant at place x</p> <p>effect at place x</p>	<p>kind or release/source spontaneous continuous gas cloud density type of terrain (houses, forest, etc.) wind situation atmospheric conditions</p> <p>acute toxicity fire/heat radiation explosion/pressure wave</p>
<b>Consequences</b>	<p>for the population</p> <p>for the environment, e.g. the ground water</p>	<p>density of population in damage area length of stay/of exposure shelter (outside or inside buildings)</p> <p>permeability of surface layers infiltration mechanisms distance to groundwater level</p>

#### 4.1 Release mechanisms and quantities released

It is assumed that prior to a severe accident, such as a failure of a substance-filled pipe system or container, some of the substance is released (with or without pressure) and that this so-called “leakage before breakage” situation, a warning signal for imminent failure, is not noticed in time.

### **Leakage before breakage situation**

Prior to complete failure of a component, e.g. sudden break or rupture of a pipeline, a crack-like leakage in the pipe can be observed. Such leakage does not open suddenly into a large hole but into cracks which grow gradually. Leakage before breakage is examined as part of the consequence analysis as described under level 2 in chapter 1.2.

The following incidents may serve as a practical guideline for the visualisation and definition of accident scenarios and accident consequences:

- A broken pipe in a pressurised or non-pressurised system with maximum mass flow rate (2F break). This is a break fully across the pipe, permitting the substance inside to discharge through both ruptured ends. With safety devices installed on both sides of the break, such as passive swing-type check valves or any other (passive) lock-up equipment, the total volume discharging from the pipe system or by action of a pump between break and closing of check valves (or other lock-up equipment) can be assessed.
- A mechanical failure of the largest container or tank, pressurised or non-pressurised. The content of the largest tank discharges either into the (largest) collecting basin or forms a puddle of assessable dimensions. It is assumed that, under certain circumstances, a BLEVE can occur in the largest tank of a tank farm for combustible liquefied gas in above-ground storage containers.
- In the case of burning solids or liquids, the quantity of substance stored within a fire-proof building compartment or in a collecting basin is to be taken as the largest interconnected quantity of substance in a plant or a store.
- In the case of an explosion of explosives, the basis is again the largest interconnected quantity of substance within the plant or the store.

With compressed or low-temperature gases it must be considered that a part of the escaped liquid will evaporate spontaneously, taking along an additional part in form of aerosols. The rest of the liquid will form a puddle on the ground of a size depending on the quantity and kind of the liquid and also on the type of surface and the possible presence of obstructions.

The rate of evaporation depends, among other things, on the surface of the puddle, the temperature of the liquid and the heat entering from the ground and the surrounding air.

The quantities released must be assessed with reference to the plant and in co-operation with the operators of the plant. Generic assessments via reference scenarios yield no useful results (e.g. no BLEVE will occur in a soil-covered tank farm for combustible liquefied gases).

## **4.2 Consequences of a release**

For the type of release in question, spreading of the released substance must be assessed as to time and surrounding. The result is a space and time-related distribution of the concentration of the released substance.

The essential factors and parameters here to be considered are described in the introduction to chapter 4. The course of spreading of a volatile substance as to time and space depends, among others, on the type of release (spontaneous or continuous), on the properties of the released substance versus its carrier medium (e.g. for gases: heavier or lighter than air), on the topography, on the atmospheric conditions, etc.

The various zones of concentration determine the zones of danger. On the basis of known criteria, e.g. the IDLH value (Immediately Dangerous to Life and Health) for acute humane toxicity, the areas dangerous to population and the environment can be specified.

For combustible substances, the possibility of a fire break-out or a gas explosion must be examined and the effect of heat radiation and the different types of explosion considered.

If a released substance flows into a surface water, the amount of water required to lower the contamination by the released pollutant to a limit not exceeding the fish or daphnia toxicity concentration, must be calculated and the possibilities for the prevention of groundwater contamination through infiltration must be examined.

When spreading on the ground is assumed, it is important to check the depth of possible penetration as a first preventive measure against groundwater pollution.

### **4.3 Consequences for the population and the environment**

The factors and parameters required for the assessment or calculation of possible damage to the population or the environment are listed in the introduction to chapter 4. Concerning the consequences for the population, it is for instance required to check on the persons supposedly staying in the danger zones and thus being immediately threatened. Several factors are here to be considered, e.g. daily variations in the density of population (day/night), shelters (in or outside of buildings) and the special vulnerability of various groups of people (children, sick or handicapped or old people)

For the assessment of environmental consequences, the most important parameters are listed in the example for the groundwater.

## **5. SELECTION OF REFERENCE SCENARIOS**

As already explained in chapter 1.2 on the impact analysis of possible severe accidents, the so-called reference scenarios qualify as level 2 of the accident consequences.

A larger “hypothetical incident” with release, fire or explosion, but clearly to be distinguished from a “horror scenario”, is assumed, with consequences comparable to that of a “severe accident” with serious danger to people and environment, as described in the Seveso II Directive.

In order not to overshoot the mark when selecting scenarios of possible severe accidents, the “reference scenarios method” was developed, which is frequently used in France and in other countries.

The selection is based on practical experience and essentially on recordings of former severe accidents with specific types of plant. Since Austria cannot avail itself of such recordings, experiences from inside the EU have to suffice. A very helpful paper is the EUR 16452 EN



Report of 1996 “Land Use Planning of Major Accidents Hazards – An Analysis of Procedures and Criteria in Selected EU Member States” by M. Smeder et al., according to which the majority of the EU member states prefers to use deterministic (consequence-oriented) methods, i.e. reference scenarios, rather than probabilistic methods.

As can be seen from this report, reference scenarios used in regional planning are primarily severe accidents with consequences reaching beyond plant premises into the near or more distant vicinity, such as

- **severe accidents with toxic consequences,**
- **severe accidents with fire and/or heat radiation,**
- **severe accidents with explosion and possible pressure wave,**

depending on the involved substance (toxic/combustible) and the manifestation of the accident (fire/explosion).

Of the accident scenarios presented in chapter 2.3.4, the following must be regarded as reference scenarios:

#### **Toxic or ecotoxic substances:**

**Toxication/pollution of surface waters and groundwater, soil contamination**

**Gas cloud without fire, heavy toxic gases**

#### **Combustible or explosive substances:**

**Puddle fire, pool fire, tank fire**

**Fire ball, boil over, BLEVE**

Burning of solids, dust explosion, jet fire, deflagration and flash fire remain unconsidered because of their comparatively minor consequences, which are usually restricted to the plant and premises.

#### **Combustible or explosive substances:**

**Gas cloud explosion, UVCE, VCE**

**Blasting materials**

For blasting materials (TNT) it should be noted that appropriate safety distances are specified in the Explosives Act.

The decomposition of explosive substances in an explosion is left out of consideration, since the consequences are usually comparatively minor and restricted to the plant and premises.

## **6. FIREBALL, BLEVE, BOIL OVER**

A fireball develops when

a container with combustible liquefied gas or a pressurised tank, holding a combustible liquid heated beyond its regular (atmospheric) boiling temperature, bursts open under the impact of (external) fire and the content suddenly expands into the surrounding pressure and ignites.

BLEVE is the abbreviation for **B**oiling **L**iquid **E**xpanding **V**apour **E**xplosion, a typical representative of accidents with combustible liquefied gases such as propane and butane.

It should be mentioned here that low-temperature storage of liquefied gases at atmospheric pressure will never cause a BLEVE.

Barrels with combustible solvents or roofed-over tanks filled with substances such as petrol can, if exposed to (external) fire, fail on account of the increased internal pressure. The result and consequences are comparable to a BLEVE from combustible liquefied gas.

A boil over occurs when, for example, the contents of a roofed-over tank is heated beyond boiling temperature and some of the contents, set aflame by the fireball of the exploded gas phase, splashes over the edge of the tank.

## 6.1 BLEVE

A container failure due to a BLEVE can be the result of two independent problems:

**Strong exposure to flames of the upper section of the container** (gas phase) leads, as result of insufficient cooling via the stored substance and the low heat capacity of the container wall, to a rapid and steep deterioration of the material properties of the container so that bursting occurs at pressures below the setting of the safety valve.

**Exposure to flames of the lower section of the container** (liquid phase) leads, as result of the vapour pressure of the stored substance, to a pressure rise inside the container. This rise is rather gradual since the vaporisation heat is transferred to the liquid only by internal heat transfer mechanisms. Critical in this connection are jet flames which can occur at a leakage in a pipe system holding a high-pressurised combustible substance. The jet of substance which forms at the exit opening is so fully turbulent that a pre-mixed flame with great heat generation is formed and, if directed against the wall of the container, will cause a large amount of heat to be transferred into the container. Heat transfers of up to  $300 \text{ kW/m}^2$  are possible and film boiling of the substance on the inside container wall is thus induced. The cooling of the wall may in the end become insufficient and the result is a failure of the container below the pressure set at the safety valve.

The sudden expansion when the vessel is ruptured causes rapid evaporation of the substance (flash evaporation) and the strong turbulence intensively mixes air into the developing vapour cloud. The successive burning of the fire ball results in an increase of pressure and an intensive heat radiation to the surroundings.

### 6.1.1 Reason for and typical course of a BLEVE

1. Leakage in the pipe system of a liquefied gas tank

2. Ignition
3. Heat rises in the tank. Initial cooling of the tank by the liquefied gas, which in turn starts to boil, whereby the pressure is raised to the point set by the safety valve. The gas released as a consequence of the pressure relief is then caused to ignite.
4. The liquid level in the tank drops till the flames hit the tank above the level.
5. The temperature of the material of the vessel raises till the vessel fails as result of deteriorated strength of material properties.
6. The tank bursts all at a sudden and the liquefied gas escapes in form of an aerosol and is ignited. The so developed fireball expands within a second to its full size, rises slowly into the air and then burns off within 10 to 15 seconds.

Large parts of the vessel fly off to distances of up to 1800 metres (see chapter 6.1.8).

### 6.1.2 Consequences of a BLEVE

For the assessment of the diameter of the fireball, known accident data were analysed and empirically correlated. TNO has derived developed a formula from the correlation which is now frequently in use:

$$D = 6.48 \cdot M^{0.325}$$

with D being the diameter of the fireball and M the mass in kg of the hydrocarbon involved (propane, butane, etc.).

The following table shows calculated diameters versus diameters reported from various accidents.

Event	Mass (tonnes)	Diameter (m) observed	Diameter (m) calculated
Celle, Germany, 1958	27	50 - 100	180
Crescent, Ill. USA 1970	64	200	240
Houston, Texas, 1971	165	300	320
Lynchburg, Virginia 1972	18	240	160
Kingman, Arizona, 1973	16	240	210
Nijmegen, The Netherlands, 1978	15	40	150
San Juan Ixhuatepec, Mexico, 1984	16 - 735	200 - 600	150 - 520

For the life of a fireball, TNO has developed the following relation:

$$T = 0.852 \cdot M^{0.26}$$

With T being the life of the fireball in seconds and M the mass in kg of the hydrocarbon involved (propane, butane, etc.).

Diameter and life of the fireballs relative to the quantity of burning propane are listed in the enclosed tables 2 and 3.

### **6.1.3 Calculation of the heat flux density**

For calculating the heat flux density (intensity) at a certain distance from the surface of the source, it is generally required to consider not only the amount of radiation and the permeability (absorption due to humidity in the air) but also the geometric form of the radiating source, i.e. the point-like, spherical, cylindrical (pool fire) or flat shape of the source.

The point source method, as indicated by its name, assumes a point-like heat source in the centre of the flame which emits a certain portion of the combustion energy in the form of radiation, of which the intensities at various distances can be calculated with consideration of the diminishing effect by the atmospheric humidity present at greater distances.

The point-source method yields satisfactory results also for spherical emitters, i.e. fireballs, and for greater-distance intensities.

The impact (on humans, peoples on duty and on materials) by radiation intensities at various distances caused by a burning propane fireball is listed in Table 1 and graphically shown in Figure 4. Intermediate values can be obtained by linear interpolation. These impact distances are conservative assessments, they are calculated on the basis of the point-source model, where incidence angle or incidence coefficient are not required to be considered. The incidence coefficient is a measure for the efficiency heat energy radiated from the heat source is registered at the exposed surface (of people, buildings, etc.) The respective impact areas, for simplicity assumed as circles with a radius equal to the impact distance, are listed in Table 2 and are graphically presented in Figure 5.

For assessing the damage suffered by the population, the impact area ( $\text{km}^2$ ) is multiplied by the respective density of population (inhabitants per  $1 \text{ km}^2$ ) of the given territory.

*With propane being a product in wide-spread daily use and hydrocarbons having a typical thermal value of 46,000 kJ/kg, i.e. the combustion of one kilogram hydrocarbon per second delivers a heat energy of about 46,000 MW, propane was chosen as reference substance.*

### **6.1.4 Impacts of heat radiation on humans and buildings**

The impact of heat radiation on humans is expressed as heat exposure or “thermal dose”. The decisive factors are heat flux density and duration of exposure.

For the assessment of the impact of heat radiation on people, a qualitative method and also a quantitative method, the so-called “probit” method, are applied.

### **6.1.5 Qualitative method**

The qualitative method uses characteristic practical data or guidelines, i.e. tables provide information on impacts caused by certain heat flux densities and exposure times.

Some reference values for the impact on people, rescue actions and buildings or equipment (“damage assessment”, Switzerland) are given below:

Heat radiation (kW/m <sup>2</sup> )	Impact on people
1	Max. exposure to sunlight
1.5	No health impairments even after prolonged exposure
4.5	Detrimental effects (formation of blisters)
6.5	Threshold of pain
12.5	First degree burns - after 10 seconds
20	Formation of blisters - after 5 second
25	Second degree burns - after 10 seconds
36	Third degree burns - after 10 seconds

Heat radiation (kW/m <sup>2</sup> )	Impact on rescue actions
1	Fire brigades have sufficient time for necessary actions and extensive checking of premises
4.5	Fire brigades need not be equipped with cooled protective clothing
8	Short actions of fire brigades with specially cooled protective clothing
12.5	Tanks can be saved when showered with sufficient water
36	Tanks cannot be saved despite extensive water showering

Heat radiation (kW/m <sup>2</sup> )	Impact on buildings and equipment
2	Destruction of lacquering on wood - after 30 minutes
3	Destruction of plastic material surfaces - after about 30 minutes
4.5	Flare-ups of bituminised roofing paper on flame contact
12.5	Bursting of glass panes - after about 10 minutes
15	Ignition of wood on flame contact; melting of plastic materials
25	Ignition of wood with no flame contact; disintegration of plastic materials
30	Distortion of sectional steel - after about 30 minutes
35	Spontaneous ignition of textiles - after about 15 minutes
36	Spontaneous ignition of wood
40	Damage to steel equipment
75	Spontaneous ignition of PVC - after 15 minutes
100	Ignition of aluminium sheet covered roof insulation; failure of load carrying sectional steel - after 20 minutes

Qualitative reference values for people, task force actions and materials are also contained in the lower part of tables 1 and 2.

### 6.1.6 Probit-method

The sensibility of persons to negative effects (heat radiation, high pressure wave from explosion, toxic gases) varies within a population, i.e. the reaction of persons to the same toxic or thermal load is not always the same. It was found that the logarithm of detrimental effects is governed by the law of normal distribution.

Incorporation of this distribution into a model (see “loss prevention in the process industries” by Lees, F.P.), has led to the introduction of the probit-function.

The general form of this function is:

$$\text{Probit} = -A + B \cdot \ln(I^N \cdot t) \quad \text{for combustible substances}$$

Probit stands for probability unit.

$I$  = heat intensity in kW/m<sup>2</sup>  
 $t$  = exposition time in seconds

A,B,N are constants of the heat radiation.

$N = 4/3$ ,  $A = 14.9$  and  $B = 2.56$  for all combustible materials.

The product of ( $I^N \cdot t$ ), often referred to in the literature as “thermal dose”, shows that the relationship between dose and effect is not linear.

With the probit quantified, the corresponding probability of casualties in percentage can be read from Figure 6, which represents the function between the casualty probabilities (in %) integrated over the normal distribution and the variable “probit”.

**Example:**

What is the probability for a person not surviving after 45 seconds exposure to a heat flow density of 12 kW/m<sup>2</sup> ?

$$\text{Probit} = -14.9 + 2.56 \cdot \ln(45 \cdot 12^{1.333}) = 3.3$$

The probability read from Figure 6 is 4%.

The values so established are conservative assessments with no protection or escape possibilities considered.

For the escape and protection probabilities, the following reference values can be used:

Heat flow density (kW/m <sup>2</sup> )	Escape or protection probability
4 - 6	0.9
6 - 13	0.5
> 13	0

This means that the percentage given in Figure 6 must be multiplied by a factor of (1 – escape or protection probability).

**6.1.7 Calculation of the explosion pressure wave (excessive pressure)**

The explosion of a released gas cloud (UVCE) is dealt with in the manner detailed in chapter 10.

### **6.1.8 Debris**

In case of a BLEVE, the tank can be torn off of its foundation and be thrown over long distances. The propulsive force develops from the counter-pressure of the burning substance discharging from the tank. The tank or even parts of it may be thrown as far as hundreds of meters. During the horrible accident at San Juan Ixhuatepec, Mexico, in 1984, 12 tanks were thrown farther than one hundred metres, one of the them even 1200 m.

It is assumed that about 60 % of the expansion energy developing during a BLEVE is converted into kinetic energy, making debris shoot through the air like missiles. The maximum shooting distance is assumed to be about 900 m for spherical tanks and about 1800 m for cylindrical tanks (see “thermal and missiles domino effects”, Delvosalle, at the European seminar on domino effects in Leuven, 1996).

Models for the calculation of the mass of debris and the respective distance thrown have been attempted, none of them, however, has so far found recognition.

## **6.2 BOIL OVER**

As already mentioned in the introduction to chapter 6, barrels holding a combustible substance or roofed-over tanks with a substance such as petrol, when hit by flames, can fail as result of the excessively raised internal pressure caused by the evaporation of the content. The result is a BLEVE with consequences similar to that caused by combustible liquefied gas.

A boil over is a splashing over of burning substance if, for example, the substance in a roofed over tank is heated beyond its (atmospheric) boiling point, causing the gas phase of the substance to explode into a fireball.

Although modelling of such type of accident is very complicated, boil over phenomena and their consequences must be considered, especially in decisions concerning the location of buildings which cannot be evacuated readily in the case of an emergency.

### **6.2.1 Pathway model**

1. Tank leakage collected in collecting basin
2. Ignition of vapour
3. Fire in collecting basin and heating up of tank
4. Tank roof fails due to excess pressure and release of gas cloud
5. Burning substance splashes into collecting basin
6. Ignition of the gas cloud leads to a fireball as described for a BLEVE and an explosion pressure wave as described for a UVCA.

### **6.2.2 Impacts of a boil over**

The fire in the collecting basin, and the burning substance splashed into the collecting basin, is a surface fire and can be treated as a “pool fire” (see chapter 7).

If ignition of the gas cloud can be expected, impacts from a BLEVE as to heat intensity and from gas cloud explosion (UVCE, chapter 10) must be assessed.

The quantity of combustible liquid contained in the released gas/air mixture can be assessed as follows:

Volume of the gas and air mixture = volume of the tank (conservative assumption)

Explosion limits, e.g. regular petrol: 0.6 to 8 vol.% (from safety data sheet)

Assumption: medium stoichiometric concentration = 4 vol.%

Released share of mass  $m_{\text{petrol}} = v_{\text{tank}} \cdot c \cdot \text{density}_{\text{air}} \cdot (m_{\text{petrol}}/m_{\text{air}})$  [kg]

$v_{\text{tank}}$	volume of the tank
$c$	concentration [vol.% ]
$\text{density}_{\text{air}}$	density of the air $\approx 1,2$ [kg/m <sup>3</sup> ]
$m_{\text{petrol}}$	molecular weight of petrol $\approx 80$ [kg/kmol]
$m_{\text{air}}$	molecular weight of air $\approx 29$ [kg/kmol]

Example:

Released share of mass  $m_{\text{petrol}}$  in an explosive mixture of a 20,000 m<sup>3</sup> petrol container ?

Released share of mass  $m_{\text{petrol}} = 20,000 \cdot 0.04 \cdot 1.2 \cdot (80/29) \approx 2600$  kg

Ignition of this vapour and air cloud develops a fireball of a diameter of about 80 m (see Figure 2) with a life of about 7 seconds (see Figure 3 or chapter 6.1.2). The impacts due to heat radiation can be taken from Table 1 or Figure 4, the excess pressure due to the explosion of the gas cloud from Table 5 or Figure 9.

### 6.2.3 Calculation of the heat flux density

The calculation is carried out analogous to the BLEVE in chapter 6.1.3, with the released share of combustible liquid in the gas cloud to be assessed according to chapter 6.2.2.

The heat flux density as result of the fire in the collecting basin can be calculated according chapter 7.5.

### 6.2.4 Calculation of the explosion pressure wave (excess pressure)

The assessment follows the explanation and directives on gas cloud explosion (UVCE) in chapter 10, the released share of mass of combustible liquid is to be considered according to chapter 6.2.2.

## 6.3 Jet fire



The burning (turbulent) jet, due to its premise-restricted impacts, – reference scenarios describe consequences at larger distances – , in general do not have to be considered. Since the jet fire, however, is important in connection with a possible BLEVE, it will be treated here briefly (see introduction to chapter 6.1). Jet fires are sometimes also referred to as torch fires or flares.

### 6.3.1 Course

A jet fire is triggered off when combustible gas, released by a hole in a pressurised storage vessel, is ignited. Typical reasons are flange or pipe leaks (corrosion, mechanical damage) or faulty pressure relief components such as safety valves, etc., which must thus not be excluded from the range of possible events described under level 1 of chapter 1.2. The destructive capacity of a jet fire (due to its high-temperature flames as result of thorough mixing with air and its intensive radiation) can cause to extensive damage in a plant.

### 6.3.2 Consequences

The assessment of the damage is complicated in as much as the place of leakage and thus the direction of the jet cannot be predicted. If the ratio between diameter and length of the flame is comparatively great, the intensity of heat radiation can be assessed via the point-source method according chapter 6.1.4; otherwise, a cylindrical model must be used.

The length of the ignited open jet can be approximated by:

$$L = 300 \cdot d$$

With L being the length of the flame in [m] and D, the (equivalent) diameter of the leak in [m].

A special case of an ignited open jet is the burn-off in the oil industry, where the length of the flare conduit must be dimensioned sufficiently long in order not to expose the nearby personnel to too strong a radiation. The length of the flame is estimated as:

$$L = 0.0177 \cdot Q^{1.08} \text{ where}$$

L is the length of the flame in [m] and Q, the heat capacity in [MW]

With 46 MJ/kg for the thermal value of hydrocarbon (see chapter 6.1.4), the length of the flame is

$$L = 1.11 \cdot W^{1.08}$$

W mass-flux flare-up rate in [kg per second].

The influence of the wind on the angle of inclination of the flame must be considered, as it can shorten the distance to the radiated object. Practical experience shows that an angle of inclination of 30° versus the horizontal can be assumed.

The issue “jet and discharge from safety valves” is treated also in the Austrian Standard ÖNORM M 7323 “erection of stationary pressurised containers for the storage of gases” or by the modification of ÖNORM M 7323/A1.

## 7. PUDDLE FIRE, POOL FIRE, TANK FIRE

When liquids and pressure-liquefied or low-temperature liquefied gases are released by a leak, the substance expands and evaporates on the ground according to the kind and shape of the surface and the heat transfer via the surrounding.

There are two types of evaporation, that of liquids with a boiling point above the ambient temperature (volatilisation) and that of pressure or low-temperature liquefied gases with a boiling point below the ambient temperature which evaporate more rapidly.

The evaporation mechanism is not a stationary process but depends essentially on the following parameters: type of release, course in time, topology and kind of ground, physical properties of the liquid, atmospheric conditions and structure of the surface.

### 7.1 Puddle area

The dimension of the puddle area is of great influence on the amount of substance evaporating and volatilising from the puddle. In most cases, free extension of the puddle is hindered by the walls of a collecting basin, for example, or by other obstacles, whereby the geometric shape of the puddle is predetermined.

If the puddle is permitted to expand freely, its size must be assessed with consideration of the respective boundary conditions. The liquid extends by action of gravity over various levels of the ground, partly obstructed by surface forces and friction, till a minimum puddle depth is reached.

Reference values of minimum depths of freely expanded puddles:

Ground	Minimum puddle depth $d_{\min}$ in [mm]
Uneven sandy soil	25 - 30
Level sand or gravel	10
Concrete or stone	5

The puddle area ( $A_{\text{puddle}}$ ) can be calculated from the released substance volume ( $V_{\text{substance}}$ ) and the minimum puddle depth ( $d_{\min}$ ) by:

$$A_{\text{puddle}} = V_{\text{substance}} \div d_{\min}$$

### 7.2 Evaporation of liquefied gases

The evaporation mechanism of released pressure-liquefied gases (typical representatives are propane and butane) follows three distinct steps.

First step:

Spontaneous flash evaporation of a certain share of the liquid, accompanied by a cooling of the remaining liquid to the boiling point at ambient pressure. The share of flash evaporation can be approximated at 20% of the amount released.

Second step:

Evaporation of the liquid droplets (aerosols) drawn along by flash evaporation due to heat transfer from ambient air. The assessment of the share of liquid drawn along and the description of the process of successive evaporation have as yet not been satisfactorily solved. The amount of liquid droplets drawn along is considered in practice by adding 50% to the spontaneously evaporated amount (rough assessment).

Third step:

Evaporation from the puddle extending on the ground by heat transfer via the ground, heat radiation (sun) and influence of the wind. This process may continue for hours.

The evaporation of low-temperature liquefied gases is governed essentially by the third step.

### **7.3 Volatilisation of non-boiling substances**

For the evaporation of combustible liquids of a boiling point above ambient temperature, the acting force stems from the diffusion of the vapour due to the vapour pressure differential between the surface of the liquid and the ambient air. The flux of substance emitted from the puddle depends primarily on the saturated vapour pressure of the liquid at ambient temperature and the velocity of the wind. Typical substances are organic solvents and different types of petrol and oils.

For assessments at level 2 (see chapter 1.2), the course in time of the flux of the evaporated mass can be neglected in the consideration. A conservative assumption is that the whole puddle has evaporated into a vapour cloud which may ignite to form a gas cloud fire or an explosion.

### **7.4 Fire**

If the mixture of vapour and air is ignited and turned into fire, the developing heat radiation is governed by the following parameters :

#### **Type of combustible substance**

The formation of smoke, depending on the type of substance, strongly reduces heat radiation. Smoke developing from hydrocarbons increases with increased C-H ratio (petrol, toluene, and similar) and smoke from C-H-O combination increases with decreasing oxygen content in the molecule (ethanol, acetaldehyde, and similar liquids).

## Size of puddle

The dimension of the puddle, if expanded freely, can be assessed as specified in chapter 7.1, and if not, it is determined by given obstructions such as the walls of a collecting basin or other limitations.

## Length of flame

The calculation of the heat flux density involves the geometric form of the emitter, i.e. the assessment of the impacts from a puddle fire is based on a cylindrical model, which is also used for impacts from a pool or a tank fire.

It is a fact that an increase in the surface of the burning substance results in longer flames and thus in increased heat radiation to the surroundings. The length of the flames corresponds to about double the diameter of the puddle (puddle fire) or the collecting basin (pool fire) or the tank (tank fire).

The length of the flame is calculated in practice by the so-called Thomas co-relation:

$$H = 42 \cdot D \cdot \{m \div [\rho_{\text{air}} \cdot (g \cdot D)^{1/2}]\}^{0.61}$$

- H length of flame in [m]  
D diameter of puddle (pool) in [m]  
 $\rho_{\text{air}}$  density of air [ $\text{kg/m}^3$ ]  
g gravitational acceleration [ $9.81 \text{ m/s}^2$ ]  
m burn-off rate of puddle substance [ $\text{kg/m}^2 \cdot \text{s}$ ]

Burn off rates measured for various substances:

Fuels	Burn-off rate in mm/min	Diameter of burning area in m
n-pentane	8.23	2.5
Premium fuel	4.4	
Diesel	2.94	
n-pentane	9.99	8
Premium fuel	4.81	
Diesel	3.33	
n-pentane	12.20	25
Premium fuel	5.21	
Diesel	3.66	
Benzene	4.4	
Solvent naphtha	3.4	
Propane	2.2	0.36
Butane	8	
Natural gas (liquid)	9.2	4.3
Hexane	7	
Methanol	3	

The burn-off rates from puddles larger than 10 – 20 m are regarded as constant.

### **Duration of the fire**

From puddle depth, calculated according chapter 7.1, and the above-listed burn off rates, the duration of a fire can be assessed.

### **7.5 Calculation of the heat flux density**

As already mentioned for the case of a BLEVE, the calculation of the heat flux density (intensity) at a certain distance from the surface of the source (puddle fire) requires, in addition to the share of heat radiation and the permeability of the air (absorption due to the presence of atmospheric water vapour), also consideration of the geometric form of the emitter, i.e. the cylindrical model of the source (pool fire).

The impact distances for characteristic heat intensities (with respect to people, actions and materials) as result of a burning puddle of isobutylene (20° ambient temperature, 50% relative humidity) are listed in Table 3 and graphically shown in Figure 7. Intermediate values can be interpolated linearly. These impact distances are based on a cylindrical flame model in which the incidence angle has been considered. A freely expanded circular puddle, 3 cm deep, was assumed. The size of the puddle can be calculated according to chapter 7.1 or is given by restrictions such as the walls of a tank or a collecting basin or other barriers. The respective impact areas, for simplicity reasons calculated for circles with a radius being equal to the impact distance, are listed in Table 4 and graphically shown in Figure 8.

The extent of damage to the population is assessed by the product of the impact area in km<sup>2</sup> and the respective density of population (inhabitants per km<sup>2</sup>) in the affected area.

Isobutylene (2-methylpropene) being the commercially most important and most often used butene was chosen as the reference substance. It is primarily used for the production of antiknock polymer gasoline and as a parent substance in the large-scale synthesising of isoprene. The thermal value, typical for hydrocarbons, is about 46,000 kJ/kg, i.e. the combustion of one kilogram per second produces a heat energy of about 46 MW.

### **7.6 Impact of the heat radiation**

The impacts are assessed again by the qualitative method or the probit method according chapters 6.1.4 – 6.1.6.

Example: Fire from organic solvents; puddle fire

During filling of a storage vessel from a tank lorry in a store for easily inflammable organic solvents (acetone, methyl ethyl ketone, methanol), the filling hose was torn open by a fork loader. Toluene flows onto the hall floor and filling is stopped after a few minutes. About 1 tonne of solvent has run out in total. The substance starts burning and a surface fire flares up.

The following consequences can be expected:

Reading from Table 3 or Figure 7, one sees:

Heat flux densities	4.5 kW/m <sup>2</sup> at a distance of 30 m from the edge of the puddle
	12.5 kW/m <sup>2</sup> at a distance of 12 m from the edge of the puddle
	25.0 kW/m <sup>2</sup> at a distance of 3.9 m from the edge of the puddle
Diameter of the puddle	12 m, - 3 cm deep

Assessment of the damage to people and to physical assets:

For the assessment of the total damage, the critical heat flux densities for people, actions, buildings and equipment, as dealt with under chapter 6.1.5, can be used.

## **8. GAS CLOUD FIRE, DEFLAGRATION, FLASH FIRE**

If a cloud of a mixture of combustible liquefied gas and air as result of

an evaporation from combustible liquefied gas released by a leak,

an evaporation from a combustible liquid released by a leak and heated beyond its atmospheric boiling point,

a release of combustible gas by a leak,

splashed volatile combustible liquid forming a puddle,

is ignited, the general result is a so-called flash fire, by which the cloud is burned off insufficiently quickly to form a dangerous pressure wave.

The smaller the cloud which drifts in the open and the less it is restricted, the higher is the probability that its ignition will result in a flash fire and not in an explosion.

Distinguished from the term explosion, the rapid burn-off of a combustible cloud is called deflagration. Appropriate tests have shown that the excess pressure developing during a deflagration is just high enough to break window panes.

The short duration of a flash fire keeps the impacts from heat radiation low and thus causes no serious injuries. Far more dangerous is the inhalation of flames, which may be lethal.

Since impacts from a gas cloud fire are usually restricted to factory premises (are of local relevance only), they do not have to be considered in the reference scenarios (see chapter 5).

## **9. SOLID SUBSTANCE FIRE, DUST FIRE AND DUST EXPLOSION**

It is not generally assumed that solid-substance fires cause immediate danger to the neighbouring population, if they occur inside buildings with closed doors and windows and switched-off air-conditioning systems. This is so because the gases from the fire become strongly diluted by thermal up-currents of the heated gases and also because fire gases usually penetrate into closed rooms only very slowly. Only very unfavourable conditions, such as a long smoldering fire and weather situations with low air exchange, may enforce an evacuation of buildings. Bad smells, even over longer distances, however, may be caused by only very small quantities of intensively smelling substances.

Dust explosions can cause casualties and great damage to buildings, generally restricted, however, to the building or the plant where they occur, and the radius of the affected area outside of the building is comparatively small.

The general procedure for the assessment of the consequences from solid-substance fires and dust explosions is described in the following.

## **9.1 Solid-substance fire**

### **9.1.1 Fire gases**

Due to the complexity of conditions for chemical reactions and the development of fires in materials stores such as a small-quantity chemicals stores and a warehouses for agro-chemicals, it is not possible to make detailed quantified statements as to amounts and rates of fire gas components.

Burning organic materials such as wood, wool, chemicals, in contact with oxygen in the air, emit fire gases. These gases, disregarding their base materials, are generally classified as respiratory toxins. Complete combustion depends greatly on the temperature of the fire, on the excess of oxygen, and the contact time (high-temperature combustion gases).

The principal components of fire gases are always carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and water vapour (H<sub>2</sub>O). In a fire involving sulphur, chlorine and nitrogen-containing substances, sulphur dioxide (CO<sub>2</sub>), hydrogen chloride (HCl), nitrogen oxides (NO<sub>x</sub>) and hydrogen cyanide (HCN) develop in different but low concentrations, depending on combustion conditions (temperature, oxygen supply, duration). Danger in the open air from CO and HCN is small; both are lighter than air.

Smoldering fires can emit unburned substances which usually settle near the source of the fire. Increased concentrations of CO have to be reckoned with.

### **9.1.2 Propagation of fire gases**

Since the true fire process behaviour is complex and determined by individual local conditions, simulating laboratory tests have proven insufficient in providing material for a detailed description or for forecasts.

The assessment of the propagation of fire gases from storage fires thus rests on the following assumptions:

Type of fire (blaze or smoldering fire)

Defined duration of the fire

Quantity of products contributing to the emission (e.g. 20% of the inventory)

Uniform release of the polluting components during the fire

The products stored in a fire lobby are a mixture of a series of differently composed items variable in time and place.

From the mean of compositions of assorted products, the development of relevant fire gases can be derived from the following example:

Mean composition of product	Composition of fire gases (per one gram of product)	
5% S	→	100 mg SO <sub>2</sub>
5% Cl	→	51 mg HCl
5% N	→	0.5 mg HCN
	→	10 mg NO <sub>2</sub>
50% C	→	23 mg CO
	→	1795 mg CO <sub>2</sub>
10% O		
5% H		
20% others		

Note:

Complete conversion of S → SO<sub>2</sub>

Complete conversion of Cl → HCl

Conversion of N into HCN and NO<sub>2</sub> according to measured values

Complete conversion of C into CO and CO<sub>2</sub> at a ratio of 2 to 98

The calculation of the propagation of the fire gases can be carried out via a suitable computation model (e.g. VDI guideline 3783, sheet 1)

A smouldering fire can emit unconverted substances. It can hypothetically be assumed that 1% of the amount of products involved in the fire will be emitted unburned, i.e. 10 mg per 1 g of products.

## 9.2 Dust fire and dust explosion

### 9.2.1 Danger from combustible dust

Dangers from fire and explosion due to the presence of combustible dust are less well known than those arising from dealings with combustible gases and liquids. Dangerous situations are thus often miscalculated.

An ignition leading to a progressive fire is, however, possible only if

an exothermically oxidative substance,  
sufficient oxygen, and  
an effective ignition source

are simultaneously available at a given place.

For setting up an explosion, these conditions must be complemented by

sufficient fineness of the combustible substance, and a  
concentration of the dust within explosion limits.

Only if all these requirements are met, can a fire break out or an explosion occur.



*According to guideline VDI 2263 (dust fires and dust explosions; hazards – assessment – protective measures, May, 1992), dust is a fine-particulate solid substance of any form, structure and density, with a grain size below about 500 µm. Dust can be a useful product or waste.*

### **9.2.2 Behaviour of dust in a fire or explosion**

If sufficiently fine solid substance is exothermically oxidative, the substance is referred to as combustible dust. The fineness implicates a large area of reaction and thus increased heat transfer (compared to non-particulate solids), and the heat loss in reaction is lower on account of the poor heat transport by the air between the grains. The contact between oxidant and dust is better and the required ignition energy is lower.

**Ignited deposited dust** tends to slow reactions such as burning, glowing or smouldering.

**Stirred up dust** (dust cloud, dust/air mixture) of certain concentrations can, however, if ignited, burn off like an explosion. Dust in the air of a concentration below 20 g/m<sup>3</sup> will in general not lead to a dust explosion.. Due to the poorer mixing properties of dust and air with reference to place and time, dust/air mixtures are never homogenous mixtures, and the upper explosion limit for dust/ air mixtures has not the same safety relevance than that for gas/air mixtures.

The explosive behaviour of stirred-up dust is influenced by the following factors:

- Fineness and concentration of the dust

The greatest effect on the intensity of the reaction lies with higher concentrations than would be expected by the stoichiometric proportion (in contrast to gas/air mixtures). The fineness of a dust can comprehensively be described only via the grain distribution. A first orientation is here often only a medium value, the medium grain size, which means that 50% of the dust is larger and 50% is smaller than the medium grain size.

- Oxygen concentration

A higher oxygen concentration results in an increased intensity of the explosion. Lowering of the concentration (e.g. by addition of inert gases) below a certain limit (oxygen limit concentration) makes dust explosions impossible.

- Pressure and temperature of a dust and air mixture:

An increase in the initial pressure causes explosion pressure and the pressure gradient to increase over time. An increase in the temperature at atmospheric pressure results in lowering of the explosion pressure.

- Water content

A distinct reduction in the intensity of an explosion can as a rule be registered with comparatively high water contents. Many products with a water content of more than 10% show a certain resistance against being drawn up by an air stream and thus do not lend themselves so easily to the formation of dangerous mixtures of explosive dust and air.

- Increased turbulence of the dust/ air mixture

Such increase leads to an increase in the vehemence of the blast

- Shape of the vessel

In long stretched-out vessels or pipelines, detonations with far higher pressures and flame speeds than in explosions can occur.

Simultaneous presence of combustible gas or vapour and combustible dust in the air

Such mixtures, so-called hybrid mixtures which, for example, can be formed in connection with the use of combustible solvents, reduce the lower explosion limit.

In conclusion, the impact of a dust explosion is essentially determined by the following parameters:

**Substance properties - characterised by the dust explosion category or the  $k_D$ -value.**

**Dust distribution - characterised by dust concentration and homogeneous or inhomogeneous mixtures**

**Vessel properties – characterised by the proportion of length and diameter and permissible reduced explosion pressure**

**Properties of the relief equipment – characterised by the area of relief and the set relief pressure and by a possibly installed downstream bleeder**

Characteristic burning and explosion data of nearly 1900 different dust categories are contained in the BIA Report 12/97 (Hauptverband der gewerblichen Berufsgenossenschaften-HVBG, Alte Heerstraße 111, D-53754 Sankt Augustin, Germany)

### **9.2.3 Impact from dust fire and dust fire explosion**

The physical, chemical and mathematical basics for pressure relief in connection with dust explosions are contained in the explanations given in VDI 3673, sheet 1, 7/95. This guideline, in addition to series VDI 2263, can be regarded as “Technology Standard”.

Calculations can be made either on the basis of nomograms of the Regulation Standard VDI 3673, sheet 1, 7/95 or quicker via the computing programme 8FEUEX, version 3.0/1995 of W.R.Klug.

## **10. GAS CLOUD EXPLOSION**

Explosion is often used as a collective term for deflagration and detonation.

**Deflagration:** Explosion with a flame propagation up to 100 m/s. This relatively low speed of propagation thus causes only a moderate increase in pressure in the zone of reaction.

**Detonation:** Chemical reaction within an explosive system with a shock wave travelling at very high speeds (of some kilometres per second to supersonic speed). Much higher pressures than in a deflagration (about 20 bar in a detonation of explosives)

When a cloud of combustible vapour is ignited, after mixing with air and forming a combustible mixture, the result can either be a slow burn-off, a flash fire (see chapter 8), or an explosion. The best known example of a gas cloud explosion is that of Flixborough (UK) in 1974. About 70 tonnes of cyclohexane were set free and the resulting vapour cloud of about 25 to 50 tonnes exploded, killing 26 people inside and 2 outside the plant. People were injured and buildings damaged in the vicinity.

The following conditions enhance the possibility of an explosion:

- Confining/tamping (full or partial)
- Large vapour volume
- Quasi stoichiometric mixture or perfect air-to-fuel ratio
- Turbulence in the burning cloud

A cloud of less than 1 tonne of vapour in the open air will scarcely tend to ignite and explode, an explosion can, however, be induced if a smaller amount is partly or fully tamped.

The reasons for the occurrence of a gas cloud explosion are primarily found in the release of combustible liquefied gases or in a leakage during pressurised processing of combustible liquids under pressure and above normal-boiling-point temperatures (Flixborough).

*In general, gas cloud explosions with an energy content of less than  $5 \cdot 10^9$  Joule (about 100 kg hydrocarbons) in the open air do not cause serious damage. For the consequences of explosions of gas clouds with an energy content beyond  $5 \cdot 10^{12}$  Joule (about 100 tonnes of hydrocarbons), however, forecastss are difficult to make due to lack of experience.*

Gas cloud explosions can be distinguished as to their immediate surroundings, they are either untamped (UVCE) or tamped (VCE) explosions.

## **10.1 Untamped gas cloud explosion**

### **10.1.1 Sequence pattern**

1. Release of a combustible pressure-liquefied gas or liquid under pressure and temperatures above the atmospheric boiling point.
2. The spreading vapour mixes with air into zones of lean and rich concentration. The rate of release and the weather conditions, i.e. wind and temperature, determine either the harmless dissipation or accumulation of the gas.
3. Ignition of the gas, either by a source of ignition onto which the cloud has drifted or by electrostatic charging and discharging at the point of release.
4. Acceleration of the flame front up to explosion speed, which is either reached or not, depending on composition and size of the cloud.

The probability of a gas cloud exploding when ignited depends, as mentioned earlier, on the following factors:

- Confining/tamping (full or partial)
- Large vapour volume
- Quasi stoichiometric mixture or perfect air-to-fuel ratio
- Turbulence in the burning cloud

### **10.1.2 Calculation of the excess pressure peak value**

The destructive impact of an explosion is derived from the “strength” of the pressure wave, i.e. the maximum pressure amplitude (peak value of excess pressure) and the duration of the pressure (positive pressure phase). If the pressure is of long duration compared to the characteristic reaction time (time of natural oscillation) of a loaded structure, the effect is quasi-static and the pressure determines the consequences. At the other extreme, when the pressure is over only a short time, the degree of destruction is determined by the impulse, the integral of the pressure with respect to the time. Although the duration of the positive pressure phase and thus the impulse of a pressure wave can be correlated with the distance from the centre of explosion, assessments of explosion impacts are usually made via the calculated peak value in the pressure wave.

For the calculation of the excess pressure peak value, several models and methods are available. The best-known ones are:

- the TNO model,
- the TNT equivalence model,
- the Kogarko/Brötz model and
- the Giesbrecht/Leuckel model.

From comparative calculations it was derived that the results obtained using the TNT equivalence model and the Kogarko/Brötz model give higher values than those obtained using the Giesbrecht/Leuckel model.

In practise, this means:

If it can safely be assumed that a possible gas explosion will have an untamped or just a slightly-tamped characteristic, i.e. be rather a deflagration with a comparatively low pressure build-up, then either the TNO or the Giesbrecht/Leuckel model should be used.

For partially tamped gas cloud explosions, the Kogarko/Brötz model or the TNT equivalence model produce realistic maximum pressure values which, however, tend to be rather too high for the immediate surroundings.

### **10.1.3 TNO model**

The impact distances (concerning impacts on people, buildings and plant equipment) listed in Table 5 were calculated with the use of the TNO model.

Intermediate values can be interpolated linearly. These impact distances are based on propane cloud explosions occurring in the open and thus can not be used for explosions inside buildings or of solid substances nor for detonations.

The excess pressure in the open air resulting from a gas cloud explosion is essentially influenced by the conditions of the affected terrain (buildings, plant facilities, walls). The impact distances in Table 5 refer to an obstructed terrain and are thus conservative values. For a terrain without obstructions, the listed distances should be shortened by a factor of 2 to 3.

Drifting gas clouds in an open terrain are practically untamped and the burn-off after ignition is a deflagration with excess pressures around 0.05 bar, just enough to break window panes.

The impact areas in Table 6 represent base areas of hemispheres of a radius equal to the impact distance.

The impact area [ $\text{km}^2$ ] multiplied by the respective density of population [inhabitants per  $\text{km}^2$ ] yields the extent of damage to the population.

Impact distances and impact areas are graphically presented in Figures 9 and 10.

**Example: Accident involving stored liquefied gas; heat radiation, pressure wave.**

A cylindrical tank of a tank farm is mechanically damaged. The result is a lateral leak in the above-ground mounted  $70 \text{ m}^3$  tank filled to 80% with pressure-liquefied propane, which is about 28 tonnes of propane. Within a short time, about half of the amount (from top to the level of the leak) of the liquid propane, which is 14,000 kg, is released. A gas cloud has formed and has ignited and the amount of propane left in the tank burning torch-like from the leak is kept under control by the fire brigade.

The following consequences have to be reckoned with:

The ignition of the gas cloud will form a short-lived fireball of high heat intensity, just as in a BLEVE and a pressure wave, as result of the low building density in the affected area, will cause only slight damage (UVCA).

Assessment of the impacts on people and buildings:

According to Figure 2, 14,000 kg of burning substance cause a 150 m large fireball with a life of about 10 seconds (Figure 3, for 14,000 kg). As shown in chapter 6.1.5, wood without direct flame contact will ignite spontaneously when exposed to a heat flux density of  $25 \text{ kW/m}^2$ . This value is reached, according to Figure 4, at a distance of 160 m from the centre of the fireball, and people in the open air will suffer first and second degree burns (see chapter 6.1.5).

The consequences of the gas explosion regarding excess pressure can be assessed from Figure 9. For 14,000 kg and a distance of about 300 m, this pressure can amount to 0.1 bar, strong enough to throw people to the ground and damage buildings (see chapter 10.1.4).

#### **10.1.4 Impacts of pressure waves on people and buildings**

For the assessment of the impact of pressure waves on people, as already mentioned for heat waves in chapter 6.1.4, two methods are in use, the qualitative method and the probit-method. Since practical examples have shown that the probit method strongly underestimates the risks caused by pressure waves, the qualitative method is preferred.

For quick orientation, qualitative reference values for people, buildings and plant equipment are also contained in the lower part of Tables 5 and 6.

The following list contains reference values for detailed impacts on people, buildings and plant equipment (“damage assessment”; Switzerland).

<b>Excess pressure in bar</b>	<b>Impact on people</b>
0.006	Storm of wind force 12
0.010	Wind (150 km/h) throws people to the ground
0.030	Possibility of slight injuries through broken glass
0.070	No injuries in open terrain
0.080 – 0.090	Wind (360 km/h) carries people away
0.170	1% of the people have a ruptured eardrum
0.190	10% of the people have a ruptured eardrum
0.210	10% of the people in open terrain are injured or killed
0.300	Casualties and injuries inside demolished buildings
0.340	25% casualties and injuries in open terrain
0.440	50% of the people have a ruptured eardrum
0.480	70% of the people in open terrain are injured or killed
0.840	95% of the people have a ruptured eardrum
1.000	95% of the people in open terrain are injured or killed 1% of the people have a ruptured lung
2.000	99% of the people have a ruptured lung

<b>Excess pressure in bar</b>	<b>Impact on buildings and plant equipment</b>
0.001	Noise immission at low frequencies (10-15 Hz) up to 137 dB
0.002	Possible bursting of large window panes, if under tension
0.003	Noise immission 143 dB, possible breaking of window panes
0.007	Possible bursting of small window panes, if under tension
0.01	Standard value for window breaking
0.02	“Safe limit”: 95% probability that no serious damage will occur at pressures below 0.02 bar Slight damage to house roofs (roof tiles) 1-10% of all window panes are broken
0.03	Limited structural damage
0.035 – 0.07	Usually, bursting of small and large window panes Occasionally, damaged window bars
0.05	Slight structural damage to houses
0.06	1% of buildings suffer structural damage 99% of all window panes are broken
0.07	Partial destruction of houses, houses may collapse
0.07 – 0.14	Shattering of corrugated Eternit panels Corrugated sheets (steel, aluminium) become detached
0.09	Slight damage to skeleton structures
0.10	Lightweight constructions collapse; pressure tanks undamaged

Excess pressure in bar	Impact on buildings and plant equipment
0.14	Partial collapse of walls and roofs of houses
0.14 – 0.21	Destruction of sand-lime brick houses and plain concrete walls
0.16	Lower limit for serious structural damage
0.17	50%-damage of masonry of houses
0.21	Slight damage to machines (1.5 tonnes) inside buildings, distorted skeleton structures torn from their foundations; 50% structural damage to civil engineering works
0.21 – 0.28	Destruction of sectional-steel lightweight constructions (without steel skeleton); ripping open of empty natural oil storage tanks
0.18	Ripping open of lightweight construction façades of industrial buildings
0.30	Severe damage to buildings (collapse)
0.34	Breaking of wooden masts; moderate damage to machines (20 tonnes) inside buildings
0.34 – 0.41	Complete destruction of houses, reinforced concrete walls break, 99% structural damage to all types of building
0.48	Capsizing of loaded railway wagons
0.48 – 0.55	Failure of 20 to 30 cm thick walls due to shear and bending forces; failure of pipe bridges (pipeline rupture)
0.62	Complete destruction of loaded railway wagons
0.7	Destruction of industrial buildings. Severe damage to machines (3.5 tonnes) inside buildings due to dislocation

### 10.1.5 TNT equivalence model

The TNT model permits easy and quick assessment of the excess pressure in an expanding gas-explosion pressure-wave. It is assumed that a deflagratively burning gas cloud and the detonative course of an explosion have a similar characteristic regarding the developing excess pressure of the resulting pressure wave.

For the assessment of the pressure, a certain part of the combustion enthalpy stored in the gas cloud is converted into an equivalent amount of TNT explosive. By reference to the known TNT relationship of excess pressure to explosion centre distance, the development of excess pressure in the gas explosion can be established.

The TNT equivalent of an untamped hydrocarbon vapour cloud is calculated as follows:

$$\text{TNT}_{\text{equivalent}} [\text{kg}] = \alpha \cdot H_{\text{CH}} \cdot M_{\text{CH}} \div H_{\text{TNT}}$$

Share of combustion enthalpy used for the shock wave (reactive mass)  $\approx 0.04 - 0.10$

$H_{\text{CH}}$  Reaction enthalpy of hydrocarbon  $\approx 46,000$  kJ/kg

$M_{\text{CH}}$  Vapour cloud mass [kg]

$H_{\text{TNT}}$  Reaction enthalpy of TNT = 4,400 kJ/kg

The excess pressure peak value with reference to a scaled distance  $z$ ,

$$z = r \div (\text{TNT}_{\text{equivalent}})^{1/3}, \text{ with}$$

$r$  being the distance from the centre of explosion,

can be taken from Figure 11.

## 10.2 Tamped gas cloud explosion

The models and methods mentioned in chapter 10.1.2 must not be used for tamped gas cloud explosions. Such explosions with excess pressures up to 10 bar can occur, for example, in fully closed vessels or buildings. The pressure increase is lower if the containment or the building is only incompletely closed (pressure relief). This implies, however, that the gas discharging from the incompletely closed space will be imparted an additional acceleration. It is not possible to establish directly applicable criteria for such situation, since too many different factors are involved.

In this connection, the basic principles of protection against explosions should be remembered here:

- Primary explosion protection - (avoidance of explosive conditions)
- Secondary explosion protection - (avoidance of ignition of explosive conditions, zoning)
- Tertiary explosion protection - (planning measures for reduction of explosion impacts)

The problems caused by closed vessels and buildings are similarly valid also for dust explosions (see chapter 9.2). Regarding the impacts of dust explosions, reference is made to the appropriate VDI Guidelines (chapter 9.2.3)

As already mentioned, there is no simple quantitative method or model available for the assessment of the consequences of a tamped gas-cloud explosion. The models referred to in chapter 10.1.2 cannot be used since far smaller quantities of explosive vapours can, when tamped, cause much more serious damage.

For assessment of the consequences of tamped gas explosions, the AutoReaGas computer programme of Century Dynamics, USA and UK, can be used. AutoReaGas is a three-dimensional CFD (computational fluid dynamics) programme solving the partial differential equations of Navier-Stokes and Euler via the method of finite elements. This software is also used in safety-technological analyses of large-scale process plants, oil platforms and mobile drilling barges in the North Sea (Robertson, N.J., AutoReaGas Users Group Meeting, Horsham, 1998).



## 11. EXPLOSIVE DISINTEGRATION

Highly reactive solid or liquid substances which are usually stored under controlled conditions can, when these conditions are disturbed, disintegrate in an explosion. Since safety-technological reasons call for storage of the smallest quantity possible, such explosions will have only local consequences and damage to people and material outside company premises is thus not to be expected.

Organic peroxide is a frequently used substance. Changed storage conditions can cause disintegration which may finally lead to a fire.

The storage of ethylene oxide requires special care (cooling). A failure in the control of the storage conditions can result in a fire with subsequent explosive disintegration.

Highly reactive substances include:

Ethylene oxide, hydrogen sulphide, acetylene, carbon-disulphide, propylene oxide, vinyl acetate, benzene.

If a substance disintegrates in an untamped explosion into the open air, the excess pressure peak value can be assessed by the TNT equivalence model (compare chapter 10.1.5). Chapter 10.2 applies if the substance disintegrates in form of a tamped explosion with excess pressure peak values being a multiple of that in an untamped explosion. A more precise assessment is not possible.

### 11.1 Explosives

The excess pressure peak value in an untamped explosion of TNT can be calculated by the method explained in chapter 10.1.5, but can also be read from Figure 11.

The excess pressure peak value following a TNT explosion, with reference to a scaled distance  $z$ , can be taken from Figure 11.

$$Z = r \div (M_{\text{TNT}})^{1/3},$$

$r$  = distance from the centre of explosion in [m], and

$M_{\text{TNT}}$  = mass of the TNT in [kg].

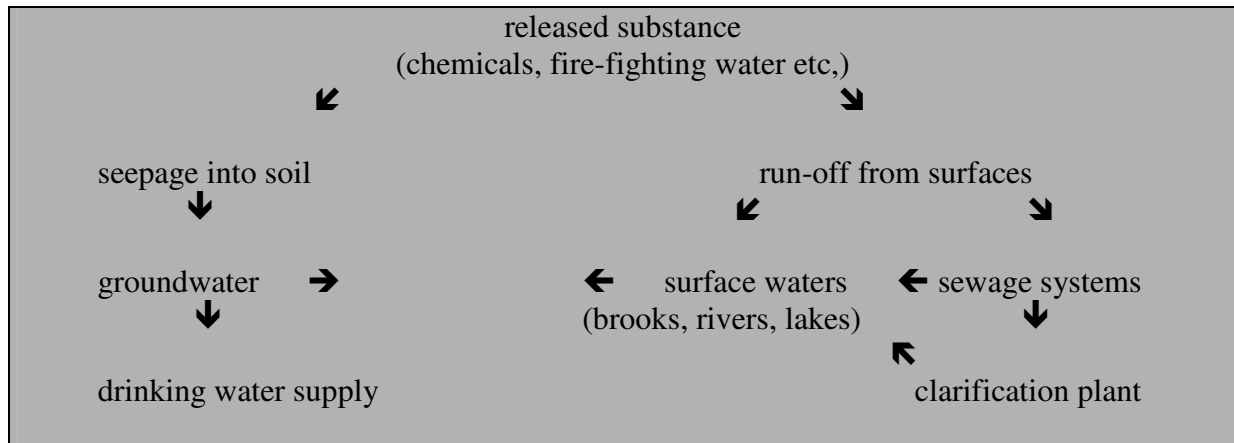
The impact of the pressure wave on people is described in chapter 10.1.4.

## 12. DANGER TO WATER AND SOIL

Natural oil derivatives, especially petrol, fuel oil, diesel and kerosene, represent the largest danger potential for environmental accidents, chlorinated hydrocarbons (CHCs) represent a large pollution potential for water and the soil.

### 12.1 Paths of propagation

When pollutants are released into waters or soils, the possible routes of propagation are shown as follows:



Since calculations for the assessment of propagation of and impacts from toxic and ecotoxic substances released into the soil and groundwater or into sewage and clarification systems require considerable effort, the selection of reference scenarios considers only propagation in and pollution of surface waters. Pollution proceeds much faster than the propagation of pollutants in soil or groundwater, and simple and quick assessments may also be made of trans-border impacts (e.g. via rivers).

## 12.2 Pollution of waters

Water-polluting substances can be categorised, according to the German Catalogue, into four water-polluting categories (WGK):

WGK 0	generally non-polluting substances,
WGK1	moderately water-polluting substances,
WGK2	water-polluting substances , and
WGK3	strongly water-polluting substances.

This classification is based on test results on toxicity to mammals, fish and bacteria, and also on the BOD (biological oxygen demand) test on characteristic biological degradation at certain intervals.

Additional criteria for environmental hazards are:

- data on mobility
- data on persistency
- data on accumulation
- direct damage potential
- indirect damage potential

For the assessment of possible impacts, it is usually necessary to distinguish between the danger to the various water or surface water systems:

- danger to surface water
- danger to groundwater
- danger to drinking water supply
- danger to sewage or clarification system

### 12.2.1 Propagation in surface waters

Contamination of waters close to the ground can be caused by:

- Transport accidents
- Trans-shipment accidents
- Overfilling of vessels (failure of overflow checks, carelessness)
- Failure of liquid separators or locks
- Leaks in or failures of vessels or connections (pipelines, hoses, valves)
- Contaminated fire fighting water, missing retaining basin.

The degree of damage done when contaminated water is released into the sewage system depends on the presence of pre-settling or retaining basins in the clarification system. If the load entering is too large, the efficiency of the biological cleaning stage will be affected or reduced to zero and the water contaminated by the accident as well as the general sewage water will flow untreated into the drainage canal. Bacteria toxicity, sewage water volumes (dilution) and control of the sewage treatment process permit a rough assessment of the polluting loads which a sewage clarification system is capable of treating.

Of decisive importance as regards pollution is the water solubility of the pollutant. With low solubility, the substance spreads out as film at the water surface (substances specifically lighter than water) or sinks as insoluble phase to the bottom (specifically heavier than water) from where it will continue to contaminate the water. The density of the contaminating substance and its solubility in water can be taken from safety data sheets.

For fuels, the following transport mechanisms must be considered: The removal of fuel from surface waters is not only determined by its biodegradation, but also by evaporation and photo-chemical degradation (quicker for volatile natural oil derivatives than for heavier ones).

As result of the degradation process, the viscosity and specific weight of the contaminating substances will increase and the components will coagulate and then sink and remain in the sediment. The oxygen-dependent biological degradation of the components in the sediment comes to almost a complete standstill.

The water solubility of mineral oil products is very low. The toxicity for living matter is not necessarily limited to the form of chemical solutions, the tiniest particles can destroy aquatic eco-systems. Moreover, thick layers of oil floating on the water surface separate the water from the oxygen in the air and thus cause oxygen deficiency in the water. The subsequent biological degradation, however, requires additional oxygen.

Chlorinated hydrocarbons, unlike natural oil derivatives, have higher densities and sink in the water. A certain part will thus seep into the soil. Some of these compounds have a high water solubility and the water is thus exposed to continuing contamination.

Without additional oxygen supply, chlorinated hydrocarbons require a very long time for their biological degradation, they are thus classified as persistent. Due to their high volatility, however, they are also quickly taken up by the air.

Computer programmes simulating pollutant propagation in surface waters are presented in the following literature:

- G. Jirka, W. Summer, “The expert system CORMIX for water quality management and hydrodynamic mixing zone analysis”, proceedings of Hydrocomp 1992, Elsevier Science Publishers LTD.
- E. Schäfer, W. Loiskandl, H. Jung, “Anwendung einer Simulationssprache zur Erstellung eines vereinfachten Alarmmodells für die Vorhersage der Stoffausbreitung in Fließgewässern”, Österreichische Wasser und Abfallwirtschaft, Heft 9/10, 1995.

### 12.2.2 Consequences of the contaminations

A qualitative overview on the damaging effects of chemicals on aquatic life is given in Table 7.

Table 8 lists essential qualitative criteria for damage potentials of a series of substance groups.

The contamination of surface waters by water polluting substances leads to an impairment of the life of plants and animals. Table 9 lists quantitative data on contaminated water volumes as a function of the amount of substance released and of water pollution category and toxicity for the aquatic life (LC<sub>50</sub> values).

For the assessment of possible consequences, additional data is required as to possible dangers from fire or explosion and to the groundwater and the drinking water supply or the sewage or clarification plant.

*The LC<sub>50</sub> value:*

This value is the mean value of lethal concentration at which, under standardised conditions, 50% of the test animals after inhalation of a toxic substance or pollutant have died. The period of exposure is stated. For the toxicity to aquatic life, only the LC<sub>50</sub> value is stated since oral uptake and inhalation of a toxic substance cannot be distinguished.

#### **Example: Manipulation with organic solvents; possible water pollution**

Careless manoeuvring of a stacker damaged 2 barrels stored in the open and thus released 400 l of trichloro-ethene. About 200 l ran into a nearby brook, 150 l, via a drain into a sewer and 50 l seeped into the soil.

The following consequences are expected:

Trichloro-ethene dissolves in water only negligibly (1,100 mg/l) and sinks to the bottom (its density is 1,5 g/ml). This solvent is strongly water-polluting with a LC<sub>50</sub> value (48 h) of 9.1 – 18 mg/l (daphnia toxicity); threshold for fish is about 55 mg/l, 660 mg/l are lethal within 15 minutes.

The substance enters the local sewage system where it creates serious problems for the biological part of the system.

The substance is hardly degradable and seeps quickly through the soil into the groundwater (even concrete cannot stop chlorinated hydrocarbons).

Assessment of the damage done to the life in the brook:

Under the assumption that 200 l of the solvent (i.e. about 300kg) ran into the brook within 20 seconds and that the flow rate of the water in the brook was 0.5 m<sup>3</sup>/s, 10 m<sup>3</sup> water (0.5 . 20) were directly polluted (1,100 mg/l, strong turbulence considered).

If the solvent cannot be pumped off immediately, it will stay on the ground till it becomes fully absorbed by the water. Considering that 660 mg/l kill fish life within 15 minutes and excellent mixing conditions of the water must be assumed, the amount of brook water contaminated by this concentration is,

$$300 \div 0.00066 = 450 \text{ m}^3.$$

Local fish mortality can be expected.

## **13. HEAVY TOXIC GASES**

### **13.1 Basic principles of gas propagation (light and heavy gases)**

The aim of propagation behaviour analysis is the calculation or assessment of immission concentrations at certain distances from the source of a given mass flow from a leakage or an evaporation.

Generally, a distinction must be made between light-gas propagation and heavy-gas propagation. The different physical propagation mechanisms of the two types of gas require the use of appropriate computing models.

The most important governing factors in propagation of gases in the atmosphere are the following:

- Turbulence of the atmosphere
- Wind speed
- Weather conditions
- Temperature layers
- Structure of the ground surface (topography of terrain)
- Buildings, obstructions
- Thermal up-currents (e.g. due to a fire).

#### **13.1.1 Heavy-gas propagation**

Heavy gases are gases specifically heavier than air. Heavy gases are predominantly pressure-liquefied gases of high molecular weight. Ammonia, lighter than air, has nevertheless specific propagation properties that are similar to those of heavy gases.

For the assessment of the amount of vapour developing from released pressure-liquefied toxic gases, see chapter 7.2.

The difference to the propagation behaviour of light gases lies in the heavy-gas cloud momentum and the very stable stratification (sharp density gradient at the rim of the cloud) inside the cloud, which obstruct thorough mixing with the ambient air.

Heavy-gas propagation occurs close to the ground, i.e. the propagation behaviour is influenced largely by the structure above ground, by houses and other obstacles, and by the wind speed. Heavy gases “flow” e.g. in the direction of gradients, even against the wind.

#### **13.1.1.1 Propagation characteristics of ammonia**

The low specific vapour density compared to air (0.6 at 20°C) implies that gaseous NH<sub>3</sub> should be drawn up into the upper layers of the atmosphere. Since ammonia, however, is very hygroscopic, the gaseous NH<sub>3</sub> and the humidity in the air form low-temperature aerosols (in the open air, not in rooms) which behave like a heavy gas, and which can be seen as fog. From a safety-technological point of view, gaseous ammonia is to be regarded as a light gas when in contact with low humidity and as a heavy gas when surrounded by regular or increased humidity. Both classifications merge into each other.

#### **13.1.2 Light-gas propagation**

Light gases are gases with specific weights approximately the same as air. The factor determining their propagation characteristic is the diffusion of the gas into the ambient air. The computing method most often used in practice is based on the propagation model by Gauss which assumes a short release of a point-like cloud at a height H above ground moving at constant velocity. The cloud is constantly thinned by admixtures of air and thus increases in volume. This process is represented in the Gauss model by a function of distribution.

#### **13.1.3 Accident-caused propagation of heavy gases**

Accident-caused propagation of heavy gases can be subdivided into:

##### **1. Combustible heavy gases**

The decisive factor to be determined is the lower ignition distance (LID) which depends on the meteorological propagation situation. In the case of ignition of the cloud (starting point for a reference scenario), either a gas cloud fire (see chapter 8) or a gas cloud explosion (see chapter 10) can be expected.

##### **2. Heavy toxic gases**

The decisive factors to be established here are the maximum concentrations and the process of concentration over time as well as the doses at fixed locations on the lee side of the source, depending on the meteorological situation affecting propagation.

### **13.2 Toxicological evaluation of accident-caused releases.**

To assess the danger potential of a substance it is necessary to have sufficient knowledge about the mode of action, targets and organs affected, and the consequences at given concentration or dose.

#### **Paths of toxic substances**

- by swallowing (oral)
- by inhaling (inhalational)
- via the skin (dermatological)

### 13.2.1 Impact of toxic substances on the human organism

#### Acute toxicity

- Characterisation of the toxicity of a chemical substance after one-time application
- No absolute measurement of toxicity
- Characteristic value: Lethal concentration  $LC_{50}$ , lethal dose  $LD_{50}$

#### Chronic toxicity

- Characterisation of the toxicity of a chemical substance after repeated application over a longer period of time (usually 2 years)
- Characteristic values: The non-effective concentration or NOEL dose (no observed effect level) or the lowest effective concentration or LOEL dose (lowest observed effect level)

### 13.2.2 Damage and mode of action

#### 1. Corrosive substances

Chemical skin burns, e.g. through acids or alkaline solutions

#### 2. Respiratory toxins

*Lung irritants*, e.g. hydrogen chloride (HCL), sulphur dioxide ( $SO_2$ ), phosgene ( $COCl_2$ )

The region affected depends on the water or lipid solubility or of the substance:

- Substances with good water solubility (ammonia, hydrogen chloride, formaldehyde) immediately affect the upper respiratory tract (throat, larynx, trachea).
- Substances with reduced water solubility (sulphur dioxide, chlorine, isocyanates) affect, after a period of latency of minutes to hours, the middle part of the respiratory tract (bronchus, bronchioles).
- Liposoluble substances (nitrogen dioxide, phosgene, ozone) affect, after a period of latency of hours to days, the terminal respiratory tract (bronchioles, pulmonary alveoli)

*Substances which obstruct the oxygen supply in the blood* e.g. carbon monoxide, hydrogen cyanide.

*Synergism*: the toxic effect of two or more chemical substances is synergistic if the total effect is greater than the sum of the individual effects, i.e. a stronger effect is registered; e.g. the simultaneous action of carbon monoxide and hydrogen cyanide.

#### 3. Cancerogenic substances:

Substances which cause cancer in the human body, e.g. benzole, vinyl chloride, asbestos.

#### **4. Mutagenic substances:**

Substances which change the genetic material of cells, e.g. acrylamide and trimethylphosphate.

#### **5. Teratogenic Substances:**

Substances which influence the physical and psychological development of the growing embryo, e.g. methyl mercury, thalidomide, ethanol, lead, toluene.

### **13.2.3 Toxicity values, limit values, reference values**

For the assessment of impacts from immissions from accident-caused releases of heavy toxic gas, which are extremely rare and short-lived, the selection of the limit values needs special consideration. Limit values based on long-term exposure, such as the MAK values, are thus not suitable for the assessment.

The assessment of acute danger as result of short-time immission exposure therefore requires the consideration of limit values which are based on exposure times of 30 to 60 minutes. Such periods are on the safe side compared with the exposures expected.

In order of significance, the following limit values can be used:

IDLH values → VCI-incidence assessment values → ERPG-3 values

#### **IDLH value: Immediately dangerous to life and health**

This value stands for the maximum concentration at which, in case of a failure of the respirator, an escape without irreversible damage to human health is possible within 30 minutes. The values are based on healthy males. There are IDLH values for about 500 different substances available.

#### **VCI-incidence assessment value:**

This value represents the concentration of a substance at which, after an exposure of up to 60 minutes, human life is lethally endangered or human health seriously and irreversibly damaged. The value is considered as a planning parameter for accident-caused damage-limiting plant layouts and as an auxiliary parameter for disaster protection measures. It is in use in Germany. There are values for about 70 substances.

#### **ERPG-3 value: Emergency response planning guidelines**

This is the maximum air-borne concentration at which almost anybody can be exposed up to one hour without any life-threatening or health-affecting consequences, immediately or in the future. The ERPG-3 value is a worst-case planning parameter beyond which, people may develop life-threatening or health-affecting symptoms. This assessment value is given preference in Germany. There are values available for about 40 substances.

The following table provides a comparison between the IDLH, VCI and ERPG-3 values for a series of toxic substances:



<b>Limit values for toxic substances in ppm</b>			
<b>Substance</b>	<b>IDLH</b>	<b>VCI</b>	<b>ERPG-3</b>
Acrolein	5	3	3
Allyl chloride	300	300	300
Ammonia	500	500	1,000
Bromine	10	0,5	5
Butadiene	20,000	20,000	5,000
Chlorine	30	20	20
Chloropicrin	4	3	3
Hydrogen chloride	100	90	100
Crotonaldehyde	400	50	50
Dimethylamine	2,000	500	500
Hydrogen fluoride	30	30	50
Formaldehyde	100	10	25
Methylamine	100	500	500
Methyl mercaptan	400	100	100
Phenol	250	200	200
Phosgene	2	2	1
Sulphur dioxide	100	30	15
Carbon disulphide	500	500	500
Sulphuric oxide, 100%	20	7.4	7.4
Sulphur trioxide	20	12	9
Hydrogen sulphide	300	300	100

### 13.2.4 Toxic concentrations and doses

**Concentration:** Unit ml/m<sup>3</sup> (ppm) or mg/m<sup>3</sup>

**Conversion of concentrations:** C [ppm] ↔ C [mg/m<sup>3</sup>]

$$C [\text{ppm}] = (\text{molar volume [l/mol]} \div \text{molar mass [g/mol]}) \cdot C [\text{mg/m}^3]$$

$$C [\text{mg/m}^3] = (\text{molar mass [g/mol]} \div \text{molar volume [l/mol]}) \cdot C [\text{ppm}]$$

Molar volume = 24.1 l/mol at 20°C and 1013 mbar

**Dose:** Unit = concentration . time = mg/m<sup>3</sup> . minute.

Dose is the share of active substance effectively absorbed by the bio-system.

**LC<sub>50</sub> : Lethal concentration fifty** (mean lethal concentration)

The calculated concentration of a substance in the breath which, over a given period of time (usually four hours), leads to a mortality rate of 50% of exposed laboratory animals.

**LD<sub>50</sub> : Lethal dose fifty** (mean lethal dose)

The calculated dose of a substance below LD<sub>50</sub> which, by application other than inhalation, leads to a death rate of 50% of a significantly high population of a defined species of animal.

### 13.2.5 Probit method

As already described in chapter 6.1.4 on heat radiation impacts on human beings, there are also qualitative reference values (IDLH, VCI, ERPG-3) for selected exposure times available, which can be used for toxicological assessments of impacts from accident-caused releases, beside the probit method for given risk criteria (casualties). In contrast to heat radiation, as can be seen from the following table for frequently used gases, the substance-related constants of the individual heavy toxic gases vary considerably.

$$\text{Probit} = A + B \cdot \ln(C^N \cdot t)$$

Probit	probability unit
C	concentration [ppm]
T	exposure time
A,B,N	substance-related constants

The product  $(C^N \cdot t)$ , the “toxic dose”, shows that the effect of the dose is not linear.

The quantified probit permits reading of the respective probability of casualty in % from Figure 6. Figure 6 is the integral of probabilities of casualties [%] with respect to the normal distribution drawn up as function of the variable probit.

Substance-related constants for various toxic gases			
Toxic substance	A	B	N
Acraldehyde	-9.93	2.05	1.0
Ammonia	-9.82	0.71	2.0
Bromine	-9.04	0.92	2.0
Carbon monoxide	-38.23	3.70	1.0
Carbon tetrachloride	0.54	1.01	0.5
Chlorine	-8.29	0,92	2.0
Hydrogen chloride	-21.76	2.65	1.0
Hydrogen fluoride	-26.40	3.35	1.0
Hydrogen sulphide	-40.35	2.90	2.0
Methyl bromide (Bromomethane)	-19.92	5.16	1.0
Methyl isocyanate	-2.97	0.70	1.0
Phosgene	-19.27	3.69	1.0
Sulphur dioxide	-23.70	1.14	3.7

These probit values derive mainly from animal experiments, their applicability to humans involves a certain degree of uncertainty. They are nevertheless useful approximation values, but should be used carefully.

#### Example:

What is the toxic dose of a release of chlorine and ammonia which will cause not more than 1% casualties ?

From Figure 6: 1 % probability corresponds to a probit of 2.7

Chlorine:

$$\text{Probit} = 2.7 = - 8.29 + 0.92 \cdot \ln(X)$$

$$X = C^2 \cdot t = 1.5 \cdot 10^5 \text{ [ppm} \cdot \text{min]}$$

This corresponds e.g. to 70 ppm and an exposure of 30 min. The IDLH value for chlorine is e.g. 30 ppm.

Ammonia:

$$\text{Probit} = 2.7 = - 9.82 + 0.71 \cdot \ln(X)$$

$$X = C^2 \cdot t = 4.6 \cdot 10^7 \text{ [ppm} \cdot \text{min]}$$

This corresponds e.g. to 1200 ppm and an exposure of 30 min. The IDLH value for ammonia is e.g. 500 ppm.

### 13.3 Models for heavy gas propagation

The atmospheric propagation of heavy toxic gases depends essentially on the following factors: release scenario (kind of substance, mode of release), meteorological conditions (wind, turbulence, topography) and the processes inside the cloud. Propagation takes place usually in the lowest layer of the atmosphere. For the assessment of the consequences of such release, a number of models have been developed.

These models have one property in common: all their calculated results exhibit a certain degree of uncertainty and errors concerning the concentrations and the volume or position of the gas cloud. The reasons lie in the incomplete physical formulation and assumptions in the model and also in the inputs relating to emission and meteorology. These uncertainties are complemented by the stochastic turbulent character of the atmosphere. Some evaluation studies have already been carried out, some are still being worked on. These studies will be dealt with in brief thereafter.

For the calculation of pollutant propagation, 4 types of models are in use:

- Gaussian trail model
- Box model
- Lagrange particle model
- Euler model

The model most used in practice is the box model.

#### 13.3.1 Typical properties of heavy-cloud propagation

Since heavy gases are specifically lighter than the ambient air, they tend to sink to the ground, once they are released. If the release happens at great height, the gas first sinks towards the ground and then spreads over the ground by action of gravity. If the release is close to the ground, the gas will immediately start to expand in this way. In the starting phase of expansion, as long as density differentials play a part, modes of propagation and mixing are primarily determined by the momentum of the heavy gas cloud. The difference in the density is steadily reduced by the mixing of gas and ambient air during the expansion, and if negligibly small, about 2% or lower, the gas continues to expand as neutral or light gas.

Neutral gas has no tendency to either rise or sink, but moves with the ambient air.

Light gases initially follow a positive thermal up-current during which they expand and mix with the ambient air until they continue to expand as a neutral gas.

### **13.3.2 Gaussian trail model**

This model is based on a simplified analytical solution of a differential equation, and is used for stationary, continuous and jet-like releases of light to neutral gases in flat terrain. It can not be used for spontaneous sudden releases.

### **13.3.3 Box model**

For spontaneous releases, a box-like model has to be used in which the initial shape of the gas cloud is described as a sphere, an ellipsoid or a cylinder of a certain given diameter and volume depending on the released quantity of substance.

The distribution of the mass inside the box is a constant or a Gaussian distribution. These distributions represent a sub-group of the box models known in the literature as “puff” models for spontaneous release.

The trajectory of the box is determined by the wind field, ambient air is mixed into the box by turbulent processes, causing a reduction in the concentration and a growth of the box. If orographic obstacles have to be circumvented, the box can be divided into several boxes.

Box models can be split into a series of boxes and thus become suitable also for releases that are continuous or variable over time.

A disadvantage of these models is that the assumed sphere or cylinder-like geometry of release does not lend itself readily for fine-structured consideration of concentration values. Up-current effects, however, can be simulated satisfactorily.

### **13.3.4 Lagrange particle model**

This model divides the gas trail or gas cloud into a large number of so-called Lagrange particles which are carried independently by the air current, on trajectories defined by wind and turbulence fields. The precision of the results of this simulation depends on the number of the particles; the computation is very time-consuming. Up-current effects on heavy and light gases are hard to describe with this model in which the particles are defined to have neither mass nor volume. The model lends itself very well to the calculation of fine-structured fields of concentration.

### **13.3.5 Euler model**

Euler models solve the transport equation via partially very complicated numerical methods. Computing is accordingly time-consuming and requires the use of main-frame computers. The advantage of this model is its flexibility, i.e. it can be used for all types of release and all kinds of gas (light, neutral and heavy).

### **13.4 Comparison and evaluation of models**

Within the last decade, ever more studies on chemical propagation models have been made in Europe and in the USA. The results obtained were compared with each other and also with field observations. The objective was and still is the avoidance of serious industrial accidents and also to obtain an overview of the increased number of available propagation models (globally more than 100 different models).

The most important findings of these evaluations in the USA and the EU are briefly described below.

#### **13.4.1 Model insecurities (Hanna et al., 1993)**

In general, propagation models will always involve a certain degree of imprecision. The reason is not only the incompleteness of physical formulation and assumptions in the model, but also the uncertain inputs concerning emission and meteorology and also the stochastic character of the atmosphere (turbulence).

The maximum expected precision was compared with field observations from 21 different propagation models, among them also 14 heavy gas models and 7 neutral gas models.

The author stresses the danger of using data of a single measuring point for the evaluation of a model, pointing out that one and the same model may produce results that are, on the one hand, 40% above the value measured at a particular point, and on the other, 40% below at another point. The comparison of models leads the author to conclude that the precision of models should be furnished with certain minimum limits which can most probably not be improved. This is to say that models with a relative deviation from the mean value of 20% and of mean square errors around 0.5 can hardly be further improved (measuring error, stochastic variation of the atmosphere).

#### **13.4.2 EPA-evaluation study (Touma et al., 1995)**

The US Environmental Authority ordered a study of comparison in which 7 propagation models were compared with the observation from 3 field experiments. The field measurements were extended up to 1 km from the source.

This study concludes that none of the 7 models examined, provided satisfactory precision in comparison with the results obtained at the various distances from the source in the different experiments. In an overall comparison, most of the results were within a factor of 2.

#### **13.4.3 Sigma Research Corporation Study (Hanna et al.,1993)**

This study compared 15 propagation models with measurements from 8 different field experiments. Just as was concluded in the EPA study, none of the models examined provided satisfactory precision compared with the results at the various distances from the source in the different experiments, and all results were within a factor of 2.

#### **13.4.4 American Institute of Chemical Engineers (AIChE, 1993)**

This institute issued a book in 1996 about guidelines on the use of propagation models concerning the release of dangerous substances. It is a model survey on 22 propagation models aimed at cataloguing the various models and their modules without specific recommendations.

#### **13.4.5 U.S. Department of Energy ( US DOE ,1997 a, b)**

Within the framework of the APAC programme (Accident Phenomenology and Consequence Methodology Evaluation), about 142 models were identified world wide which may be applied for propagation computation. No comparison were made between results from models and data from experiments. The primary purpose of the study was the identification of models, by the use of defined criteria, which can be recommended for danger assessments. From a list of 24 examined non-commercial models, 4 were recommended for the assessments of scenarios.

#### **13.4.6 European Union**

The activities in the EU on the evaluation of models of the propagation of heavy gases started in 1992, with the foundation of Model Evaluation Group (MEG) by the Directorate General XII. The "Guidelines for Model Developers" and the "Model Evaluation Protocol" were published by them in 1994. A group of experts, the "Heavy Gas Dispersion Expert Group" (HGDEG), nominated by MEG in 1993, prepared the REDIPHEM study (Review and Dissemination of Physical Effect Models) between 1993 and 1995.

All the then current European propagation models were examined. In addition to general aspects and a detailed description of the models, the study provides an evaluation protocol in which the basics of the individual models are presented. No direct recommendation for a certain model, however, is given.

In order to be able to compare the models in the future with measurements from the field, the REDIPHEM database for altogether 10 independent different field experiments was set up.

In the EU since 1996, subsequent to the REDIPHEM project, the most comprehensive study regarding evaluation of heavy gas models, the SMEDIS project (Scientific Model Evaluation of Dense Gas Dispersion Models), co-ordinated by the UK Health and Safety Executive and Electricité de France, is under way. All current European models, totalling 25, will be examined on the basis of the general evaluation protocol HGDEP (Heavy Gas Dispersion Evaluation Protocol). The papers for this project will probably be concluded and published by 1999.

#### **13.4.7 Conclusion**

The model comparisons of US studies have so far shown that calculated and measured results deviate by a factor of up to 2. As to the precision of models, it is concluded that, due to measurement errors and stochastic changes of the atmosphere, there are certain limits which can scarcely be improved; deviations from the mean value in both directions are around 20%.

The results of the SMEDIS study as to the precision of the European models are at present not available, but will probably be comparable with those in the US studies.

It is thus natural to focus on the models used by our neighbours, in Germany and in Switzerland.

### **13.5 Comparison of models; Germany and Switzerland**

For heavy gas propagation in Germany, VDI guideline 3783 sheet 2 is declared state of the art technology and model DEGADIS was accepted (by resolution of the *Länder* committee for immission protection LAI,1987 as the computation model. DEGADIS ranks high in US evaluation studies and is used by many organisations for assessing the development of heavy gas concentration after an accidental release.

In Switzerland, the so-called MET model (model for effects from toxic gases) has been used for more than 10 years for impact computation in connection with the release of heavy toxic gases. Its use is simplified by the results being easily readable from tables or calculable via a computer programme.

### **13.6 Recommendations for application**

#### **13.6.1 VDI Guideline 3783**

The VDI Guideline is simple and user-friendly and permits ready application of the model, i.e. it has only a few error sources, in the data input and in the interpretation of the results. It permits a rough assessment of the propagation of heavy gases, using considerably simplified assumptions (e.g. no consideration of the thermodynamic processes during the development of the heavy gas cloud).

The simplifications mean that, as regards the configuration of the source, only data on released mass, duration of release and density of the gas are taken into account, which makes results for points close to the source susceptible to errors.

When sheets 1 and 2 have to be combined, the results must be treated with much scepticism. The difference in the two computation models (wind tunnel tests, Gaussian expansion formalism) lead to a propagation situation which is physically impossible.

Comparison with observations from severe accidents show that using the VDI Guideline may produce exaggerated as well as underestimated concentrations.

#### **13.6.2 DEGADIS**

DEGADIS (dense gas dispersion) is a heavy gas expansion model, developed by the University of Arkansas for the American Coast Guard, for gas dispersion in flat unobstructed terrain.

The important phases of heavy gas expansion considered by this model are:

- Formation of the heavy gas cloud after release
- Expansion by gravity with mixing of air by momentum of the cloud
- Phase of heavy gas expansion with mixing of air by currents and turbulence of the atmosphere
- Transitions of expansion as tracer substance (continuous transition from heavy gas to tracer gas)

The calculation of the expansion behaviour is suitable for close, medium and far-distance areas. DEGADIS permits connection to on-line measured meteorological data. Comparison with observations from severe accidents showed that this model yields realistic assessments of actually expected pathways of concentration.

### **13.6.3 MET model**

This model describes releases of gases and gas mixtures. Fire and transition into aerosols close to the source are considered. The expansion is calculated via a box model distinguishing between heavy, neutral and light gas behaviours. The concentrations inside rooms are assessed. The result is expressed in terms of toxicity. The database of the computer version contains data on 480 chemical substances. The wind field is horizontally constant. The turbulence is considered according to 7 categories of stability (expansion classes A to G). As is also the case with all other models, complex topography cannot be considered.

The model calculates the toxicity (IDLH value, MAK value, LC<sub>50</sub>, LD<sub>50</sub>) as a function of the quantity released over distances of up to 20 km.

The model was developed especially for task forces and disaster countermeasures. It is very useful for consequence assessments. Its applicability was tested by data recorded from more than 20 incidents in chemical plants.

### **13.6.4 Conclusion**

Based on the fact that

- the MET model has been successfully used in Switzerland for more than 10 years,
- the topography of terrain considered in the expansion calculations is similar to that in Austria, and
- the tabular form of presentation of results is very user-friendly,

it is recommended to use the MET model initially and, after having analysed the findings of the European SMEDIS study, to consider a possible switch to other models.

## **13.7 Expansion and consequences according to the MET model**

The basis of the impact distances and areas listed in Tables 10 to 13 is the “technical tool for protection against C-accidents”, MET model for effects involving toxic gases, Centre of Defence, Bern (“Technischer Behelf für den Schutz bei C-Ereignissen”, MET-Modell für Effecte mit toxischen Gasen, Zentralstelle für Gesamtverteidigung, Bern).

As a simplification for accidents of this kind, it is assumed that the release is spontaneous (puff model), i.e. that the release is not a continuous process over time.

The conservative assumption is that a release takes place without fire under conditions equivalent to propagation class D (no fog and a wind speed of more than 5 m / s) and a release takes place with fire, equivalent to propagation class C (fire, no fog, a wind speed of more than 5 m/s). Both tables are based on an angle of dissipation of 60°.



For the use of the tables, only two parameters are required, the amount released (with consideration of chapters 7.2 and 7.3) and the toxicity value (IDLH value, chapter 13.2.3). Intermediate values can be derived by linear interpolation.

The impact distances in [m] from the centre of the accident are valid for persons in the open terrain, 10% of whom will suffer detrimental effects to their health on account of the released substance. Annoyance through odours, which can extend to far wider distances, is not included in these effects.

The damage to the population is assessed via the impact areas in tables 11 and 13 which, for simplicity, are presented as a 60° sector of a circle of a radius equal to the impact distance.

The total damage is the product of impact area in [km<sup>2</sup>] and density of population in [people/km<sup>2</sup>] in the affected area. The result quantifies the number of people affected (health damage to 10% of the population).

Impact distances and impact areas are graphically represented in Figures 12 to 15.

### **Example:**

Assessment of the consequences of a release of 60 kg liquid chlorine :

According to chapter 7.2, about 20%, i.e. 12 kg, evaporate spontaneously and about 50% thereof, i.e. 6 kg, are drawn up as aerosols. The remaining amount of 42 kg spreads over the ground and forms a liquid puddle.

The IDLH value of chlorine is 30 ppm. Converted to [mg/m<sup>3</sup>] according chapter 13.2.4, this yields a chlorine molar mass of 70 g/mol and an IDLH value of  $\approx 85 \text{ mg/m}^3$ .

From Table 10, for a rounded up amount of 20 kg and a rounded down IDLH value of 20 mg/m<sup>3</sup> (pessimistic assumption), the impact distance is 245 m. From Table 11, the corresponding impact area is read as 0.03 km<sup>2</sup>.

With a mean population density of about 1300 people/km<sup>2</sup> (about urban density), 39 persons (1300 . 0.03) are affected or 4 (10%) of them are expected to have suffered bodily harm.

### **Example:**

Assessment of the consequences of a release of 60 kg liquid ammonia.

According to chapter 7.2, about 20%, i.e. 12 kg, evaporate spontaneously and about 50% thereof, i.e. 6 kg, are drawn up as aerosols. The remaining amount of 42 kg spreads over the ground and forms a liquid puddle.

The IDLH value of ammonia is 500 ppm. Converted to [mg/m<sup>3</sup>] according chapter 13.2.4, this yields an ammonia molar mass of 17 g/mol and an IDLH value of  $\approx 350 \text{ mg / m}^3$ .

From Table 10, for a rounded up amount of 20 kg and a rounded down IDLH value of 350 mg/m<sup>3</sup> (pessimistic assumption), the impact distance is 100 m. From Table 11, the corresponding impact area is read as 0.005 km<sup>2</sup>.

With a mean population density of about 1300 people/km<sup>2</sup> (about urban density), 7 persons (1300 · 0.005) are affected or 1 (10%) of them is expected to have suffered bodily harm.

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## 14. LITERATURE

### ANNEX (TABLES AND FIGURES)