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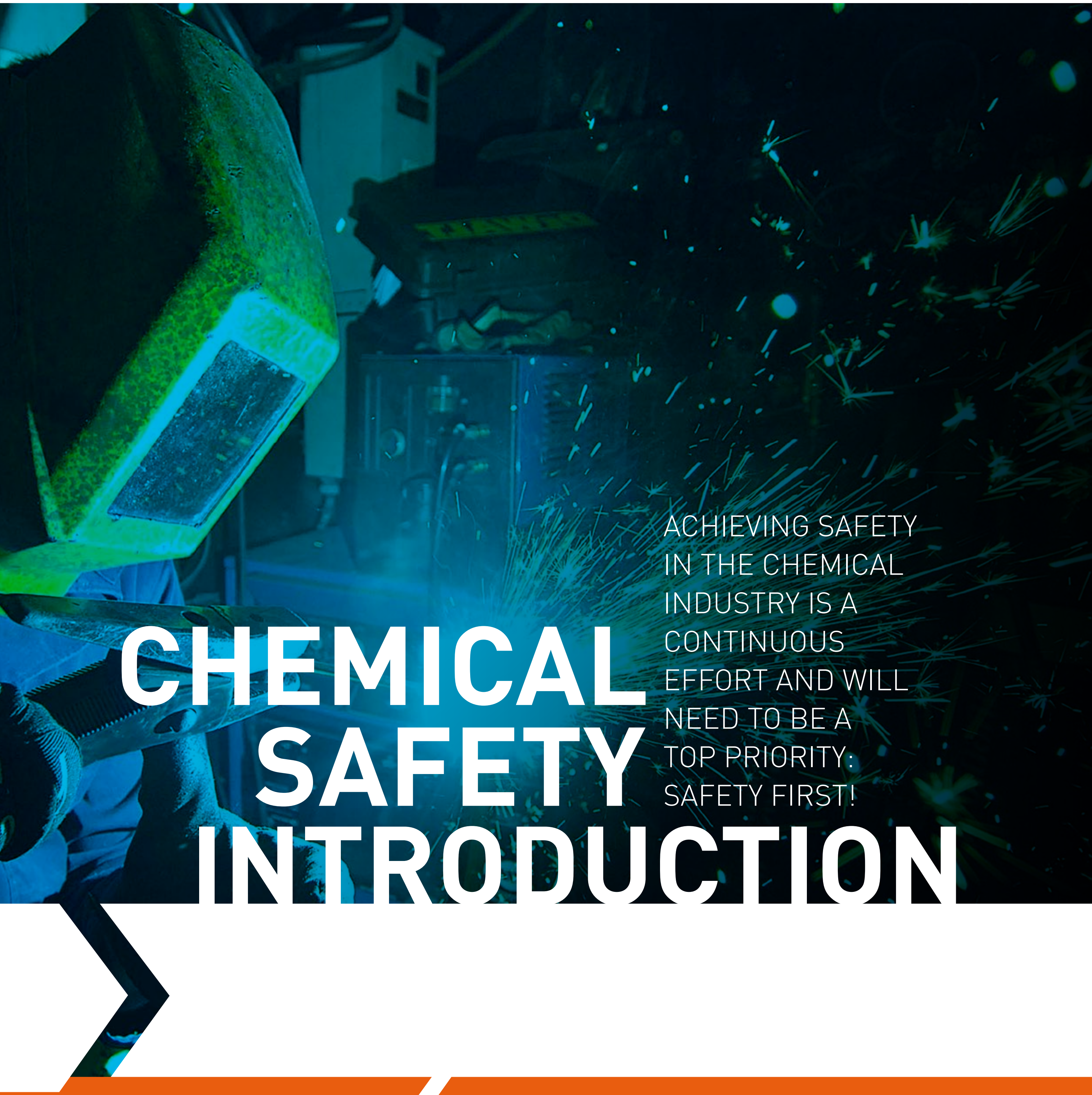

# CHEMICAL SAFETY INTRODUCTION

ACHIEVING SAFETY IN THE CHEMICAL INDUSTRY IS A CONTINUOUS EFFORT AND WILL NEED TO BE A TOP PRIORITY: SAFETY FIRST!

**Ir. P.M.M. Goossen**

# Chemical Safety Introduction

Ir. P.M.M. Goossen, March 2017

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# 1. Introduction

## 1.1 Risk, Hazard and Safety

These words are often used interchangeably by people trying to describe aspect of safety or unsafety but they are not the same. In fact they describe very different aspects.

A **Hazard** is defined as something with the potential to cause harm. It is the negative side of an activity or situation. This could be a physical property for example: a liquid on a temperature of 200 C has the potential to cause severe burns so a liquid at that temperature in principle is hazardous. It could also be a hazardous interaction with the human body for example: carbon monoxide molecules bind to the hemoglobin in the blood replacing oxygen and as a consequence the organism may die from lack of oxygen. A hazard therefore is always present as it results from intrinsic properties of a substance or situation. A hazard assessment is aimed at finding the potential to cause harm in a given situation.

A **Risk** on the other hand is a chance. The likelihood (or chance) of harm in defined circumstances. For a risk you have therefore 2 elements: a hazard (or harm) and the likelihood that it will actually happen. Consider for example smoking: several substances in cigarette smoke may cause cancer but there is a chance that it will not happen at all. Therefore if someone is exposed to cigarette smoke he or she takes a chance on harm ( .. is “at risk”). A risk assessment is aimed at finding the chances on harm done.

So what is Safety then?

**Safety** is a practical certainty that no harm will be done. In terms of risk and hazard: safety is the situation in which the risk on negative effects of a hazard are acceptably low. This is subject to interpretation; what is acceptable for one person would not be acceptable to another or for a whole group. One can also conclude that 100 % safety is only possible if there is no hazard at all. Practical safety on the other hand indicates that the chances on the harm are sufficiently low. This can be achieved by creating a situation in which the chances on harm are low enough or by protecting against the harmful situation thus lowering the chances of adverse effects.

To arrive at a safe situation means arriving in a situation in which the risk is sufficiently low. This can be achieved in different ways. For starters one can try to avoid the risk altogether. If that is not possible then we can try to control the risk or protect against it. And if the protection fails we need to save ourselves. These four stages, *avoid, control, protect and save,* are defining the four prevention classes in safety science.

**Zero-order prevention: Avoidance**

The use of the number zero in the naming originates from the fact that protection from the risk can only be achieved by *not* executing the activity. For example: in the chemical industry a solvent is not / no longer used because of its big flammability risks. However, if the solvent is replaced by a non-flammable solvent one needs to also take into account the risks associated with this new solvent.

**First order prevention: Control.**

Control of risk is the most fundamental way to achieve safety. Here we are talking about measures that may prevent the accident or damage – the negative consequence- from happening. A fuse in an electrical circuit for example prevents the system to be overloaded with so much current that a hazardous situation occurs.

**Second order prevention: Protection.**

If a situation remains unsafe despite first order prevention measures then one needs to protect him/herself against harm done. Examples are protective clothes, earplugs or a helmet.

**Third order prevention: Rescue.**

Prevention measures of the third order are no longer aimed at avoiding harm done but instead are aimed at minimizing the effects or the damage. Typical examples are the ambulance who tries to rescue a victim or the fire department rescuing people in fire situations. On larger scale these measures exist as well; for example local governments have emergency plans and evaluation plans in cases of disaster.

In this syllabus several different aspects of hazard, risk and safety related to (working with) chemicals are covered:

1. Safe Behavior: this section explores the influence of behavior of people on (un-)safe situations. It looks at the influence of antecedents preceding the behavior and the consequences of that behavior on the behavior itself.
2. Basic Toxicology, Exposure and Risk assessment: In this section it is explored how substances may interact with the human body and how they may cause harm. Equipped with knowledge on the adverse effects of substances and how (and how much!) they have entered the body it becomes possible to assess the risk of exposure to that substance in a given situation.
3. Fire & Explosions: fires and many types of explosions are in essence both results of oxidation reactions. Various aspects of fire- and explosion hazards are discussed.
4. Safety aspects of producing chemicals and Risk assessment: what techniques are used in design and operation of chemical plants to prevent hazards and methods to find and evaluate potential hazardous situation which might occur. Then, once hazardous scenarios are known, how is the risk associated assessed (properly)?
5. Safe handling of chemicals: handling and transportation of substances and chemical products are as essential to the chemical industry as the production in chemical plants is. This section covers classification and labeling of chemicals and transportation safety aspects.
6. Incident analysis: when an incident occurs the question rises “why did this happen?” and also “how can we prevent this from happening again?”. A proper incident analysis may provide the answer to both and this section covers how to do an effective incident investigation so that valid lessons may be learned and shared.

# 2. Safe Behavior

## 2.1 Incident Statistics

Safety incidents in the chemical industry can be divided into two different groups:

1. Incidents resulting in adverse effects to one or more human beings
2. Incidents resulting in adverse effects on the environment

The first group is a large group that may involve very different types of incidents, for example: a toxic cloud release may cause health effects for the inhabitants of an entire city, or a worker in a plant hurt himself while trying to complete his task, or …..

The second group involves all negative or adverse effects that the incident can have on "the rest of the planet"; animals, plants, or any other living organism. But these effects may also impact human health, for example: if a chemical is released to a river in which the fish get exposed to it, it may very well be that humans get exposed to that very same chemical if the fish get caught and subsequently eaten.

In the chemical industry, like in most other industries, there is a general drive to reduce the number of safety incidents to a level as low as possible.  After all, a relatively small incident happening in a chemical plant may sometimes result in a very big disaster like a catastrophic explosion. The history is full of catastrophic events that occurred in some chemical plant in the world. So how do we prevent these incidents that may cost lives?

The statistics of all incidents happening, big and small, have been studied on many occasions and in many companies. In general they classify incidents in different groups depending on the severity of the result, from incidents resulting in a fatality, through a category of reported serious injury and minor injury to categories that involve no injuries (yet); this last group often is referred to as "near misses"; incidents in which people say for example: "it was pure luck that no one got hurt!"

If companies record all incidents happening and add up how many of each category they find then the result looks something like the pyramid in Figure 1.

This pyramid is based on actual statistical data and suggests that for every 2 million unsafe acts statistically one of them leads to a fatality, 400 will result in reportable or major injury, and 10.000 of them will result in a minor injury.

One way of using this information is: by measuring how many near misses are occurring one could predict how often a fatality of injury can be expected.

But more important is the conclusion that at the base of this pyramid there is one thing only: unsafe behavior of people. After all, humans aren't always acting in a safe manner. And obviously the fact that statistically there is only a 1: 2.000.000 chance that your unsafe act will lead to your death doesn't help improving people's behavior in that respect either.

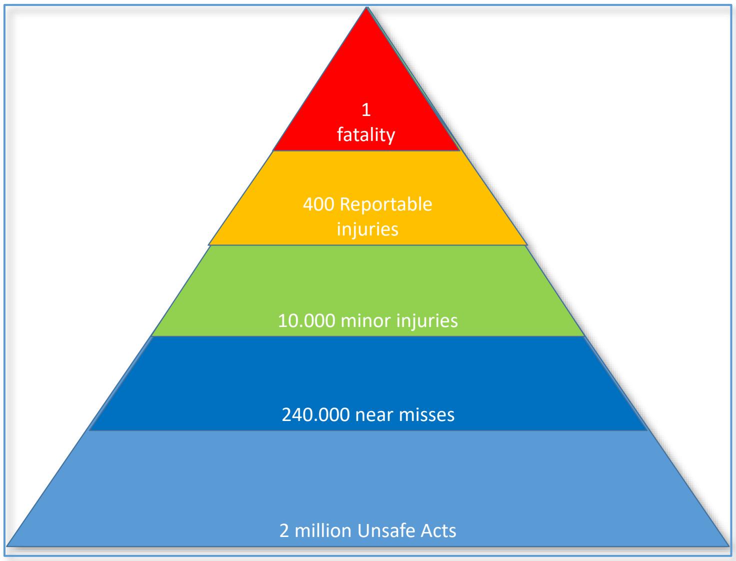


*Figure 1 : incident pyramid*

However, considering how many actions are carried out in a chemical plant by the people at work every day it is also easy to see that the 2.000.000 acts aren't at all hard to reach, especially in a very large company with many employees.

Looking at the pyramid it seems clear that the only way to truly get safety performance of a company up to world class standard is by trying to minimize the number of unsafe acts people do. But how?

## 2.2 Influencing behavior of people

In the previous chapter we were left with the question how to change people's behavior so that unsafe acts are no longer done. The science of human behavior is not an easy one, more so because humans aren't all the same; what effectively changes behavior of one person may be totally useless for another.

One of the questions that is prominent with people working in safety departments is "How can we make people do something that they do not want to do?"

For example: how do we make sure everyone in our plant always wears his helmet?

Well, the answer to the question how to make people behave differently than they want has no easy answer, but we do know that we need to find the right set of Antecedents and Consequences that will influence a change in behavior. This is the basis of the so called ABC-model; a model used to analyze human behavior and their influences. ABC stands for: **A**ntecedents, **B**ehavior and **C**onsequence

The ABC model of influencing behavior therefore has three parts as shown in Figure 2.

*Figure 2: Core Model of Influencing Behavior: ABC-analysis*

**Antecedents** come before the actual behavior, they indicate what behavior is needed and trigger the behavior (good or bad) to occur. Examples of antecedents are alarm clocks, company policies, training manuals, ringing telephones, memos but also hunger, fatigue, lack of social contact or desire for recognition.

Antecedents can be weak or strong. Some examples of very strong antecedents are addictions, habits, instincts, personality or consequence history. This last one  can be illustrated by this example: if someone crosses a railway track 100 x every day and there is never a train coming then after some time this person will stop watching if a train is coming at all (since no train will come anyway?) which in turn is an unsafe act for that particular activity.

Typical antecedents often seen in professional working environments are trainings, pep-talks, actions on a to-do list, a stated goal, a meeting request.

Understanding antecedents is important because they will tell us what is important or expected. They derive their power however from the consequences they are associated with. In case of an alcohol addiction for example the associated consequence is a desired state of mind. Absence of this state of mind will drive the addictive person to show behavior that will generate the desired state again.

Some antecedents can come from within the person (e.g. physical conditions and dispositions).

Interesting is that managers, in order to influence behavior, spend most of their time and effort on creating antecedents but when used alone, so without a paired consequence, they only have a short time effect. The strongest effects of antecedents are found when paired with a fitting consequence; that starts a desired behavior.

**Behavior** of people is something measurable, observable. It is factual. The things people say or do, or the things they do not do are all part of the behavior. In order to understand the behavior one has to measure that first and that can only be done by observing.

However, a good observation is not easy to do. For an effective ABC analysis the observation of the behavior needs to be NORMS based, meaning:

- <u>N</u>ot an interpretation: many times when people observe others they tend to describe the behavior they see including the interpretation of what they believe is behind it, but a good observation is free of interpretations. Example: observing a taxi driver at work the observer states" "the observed person tries to avoid a collision by steering to the left". This observation includes an interpretation as the observer assumes a reason behind the actual observed behavior: "the driver steers to the left" would be more appropriate.

- **O**bservable: this means that the observation is, as it says, actually observable. "the observed person thinks he is doing the right thing" would not qualify as a thinking process cannot be observed as such."The observed person explained his behavior as he was thinking it was the right thing to do" would be better as the observation in this case is the actual (spoken) explanation of the observed person.
- **R**eliable: this topic is often discussed in various detective television programs as witnesses of a crime are tested if their observation is actually reliable. An example of unreliable observation would be: an observer is observing the behavior of a person at work but he, the observer, is actually the direct boss of the person observed. This dependence will influence the behavior of the person observed as he/she tends to show only wanted behavior and not actual behavior.
- **M**easurable: a measurable observation for example is counting the number of people wearing their helmet at work in a plant. If it cannot measured it is likely that whatever you try to observe is not actual behavior but something else (interpretations etc.)
- **S**pecific: a specific observation is an observation done in a specific setting or environment. The results cannot be translated to another situation easily. For example: observing how many workers wear a helmet at work will not give any conclusion on how many people will wear a helmet in other situations. Just think of driving a motor cycle: the percentage of people wearing a helmet in that situation will be significantly higher than if you would try to measure how many people wear helmets at home.

Good observations are the basis of a good ABC analysis. They will give insight in the actual behavior of people in a given situation. That in turn creates the opportunity of changing this behavior with antecedents and consequences while using the same measurement of behavior to record progress in that change.

**Consequences** are events that follow behavior and influence the probability that the behavior will occur again in the future. Examples are: Getting a ticket for driving too fast, Praise and recognition from others or Feeling proud about your work. Consequences are defined by the effect they have on the performer's behavior, not by the giver's intentions; rewarding someone for work that was well done by giving him/her another, more difficult task may be a good consequence for an ambitious person but a very bad consequence for someone who is not. Consequences therefore have to be appropriate for all (or at least most) of the people whose behavior needs to change.

In order to have a powerful effect a consequence needs to

- <u>happen soon after the behavior</u>; if the effect one someone's behavior is not felt for some time it will no longer be linked to the (undesired) behavior and hence will not change this behavior.
- <u>be important to the performer</u>; it is obvious that without importance the person will not care either way with respect to the consequence and hence it has no effect on the behavior.

- <u>have a high probability of occurring</u>; if there is a big chance that nothing (bad) will happen when performing an undesired behavior then the performer will "take the risk".

So, when thinking of adding consequences to a given situation in order to influence behavior it is important to understand the effect of the consequence – does it *encourage* or *discourage* the behavior?- , the timing – is the effect *immediately* felt or is it *delayed*? -, the importance - Does the performer *care a little* or *care a lot* about the consequence? – and the probability - From the performer's perspective, is the consequence *likely* or *unlikely* to occur?

Consequences come in four different form as shown in Figure 3.

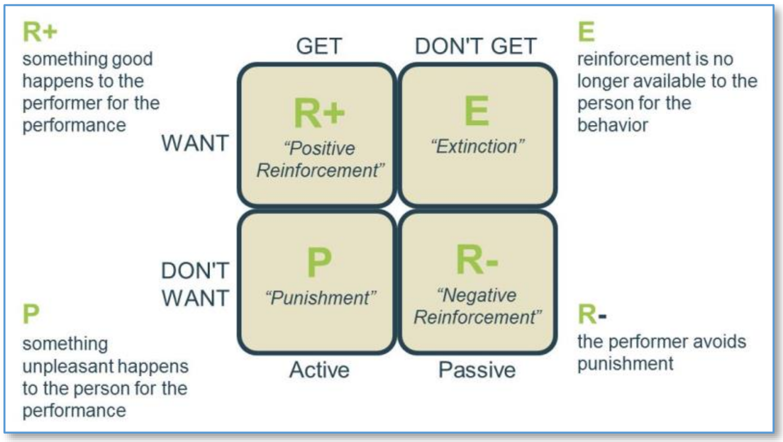


*Figure 3 Types of consequences*

All of these consequences can have an effect of the behavior but it will depend on the specific circumstance which one would result in the biggest behavioral change.

In order to create a safer working environment using ABC analysis 3 steps have to be taken:

1. Observe the situation: record the situations observed and the behavior of the people in that given situation.
2. Analyze the situation: try to identify potential hazards and dangers, analyze antecedents applicable and define expected behavior based on those antecedents
3. Change the situation: in case of dangerous situations change the way the work is done to avoid the hazardous situation altogether and/or change behavior of the people in the situation by pairing consequences to the (wrong) behavior.

# 3. Toxicology, Exposure and chemical risk assessment

## 3.1 Basic toxicology

Many years ago toxicology was defined as the science of poisons. However, the exact definition of a poison was missing. Paracelsus in the 15th century stated the problem as follows: “All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy”. He was right. Harmless substances, such as water for example, become fatal if delivered to the biological organism in large enough doses. On the other hand; there are numerous examples of substances that are considered a poison but have a healthy effect in very low doses. A fundamental principle of toxicology is

> There are no harmless substances, only harmless ways of using substances.

Today, toxicology is better described are the qualitative and quantitative study of the adverse effects of substances on biological organisms. In other words; toxicology may be described as "the science that defines limits of safety of chemical agents".

Toxicologists work in various different fields:

*Clinical Toxicologist*; concerned with the effects of chemical (drug) poisoning and the treatment of poisoned people. A clinical toxicologist in essence is a doctor who wants to know and understand how to cure people who have been “poisoned”.

*Descriptive Toxicologist*; concerned directly with the toxicity-testing of chemicals. It is a difficult task to design a good toxicological test. For example; testing toxicity on, say, birds may not give an appropriate answer to the question if the substance is toxic to humans.

*Environmental Toxicologist*; concerned with the ultimate environmental fate of chemicals and their impact upon the biological ecosystem and human populations.

*Forensic Toxicologist*; concerned with applying techniques of analytical chemistry to answer medico-legal questions about harmful effects of chemicals.

*Industrial Toxicologist*; concerned with disorders produced in individuals who have been exposed to harmful materials during their course of employment.

*Mechanistic or Biochemical Toxicologist*; concerned with elucidating the biochemical mechanisms by which chemicals exert toxic effects.

*Regulatory Toxicologist*; concerned with assessing descriptive data with regard to the risk involved in the marketing of chemicals and their legal uses.

Once substances have entered the body they may interact with it causing all kinds of adverse effects. These effects may be

- acute or chronic,
- immediate or delayed,
- irritating or permanently damaging,
- affecting the whole body or just parts of it or specific organs,
- permanent or reversible, or
- Affecting the person exposed or his/her off spring.

The same in principle applies to living organisms other than humans. In that case we state that the substance is toxic for the environment.

## 3.2 Dose / Response

As stated by Paracelsus, - the dose makes the poison - for a given substance we can determine the dose that will kill a certain percentage of a population. Most commonly the dose at which 50 % of mortality occurs is used as a measure: the LD50. (LD stands for lethal dose)… or LC50 (LC = lethal concentration) in case of vapors and gases.

The units in which the LD50 is given is usually mg (of the substance per kg of bodyweight (of the organism exposed). The LD50 dose is therefore corrected for the actual bodyweight of the organism exposed. This is done because it has been observed that smaller bodies will need lower amounts of poison to create the same effect, which most people actually know already as on every medicine bottle it is made clear what doses should be used for adults and for children. Children need a much lower dose to show the same effect.

The LD50 is actually only one point on the so called dose/effect curve. This curves describes the effect a certain dose has on the population of organisms. So it consists of all kinds of “LD’s” : LD10 (dose which results in 10 % mortality), LD20…. Etc etc. In other words: it shows the relationship between the dose of a chemical and the anticipated incidence of an adverse health or environmental effect in an exposed population.

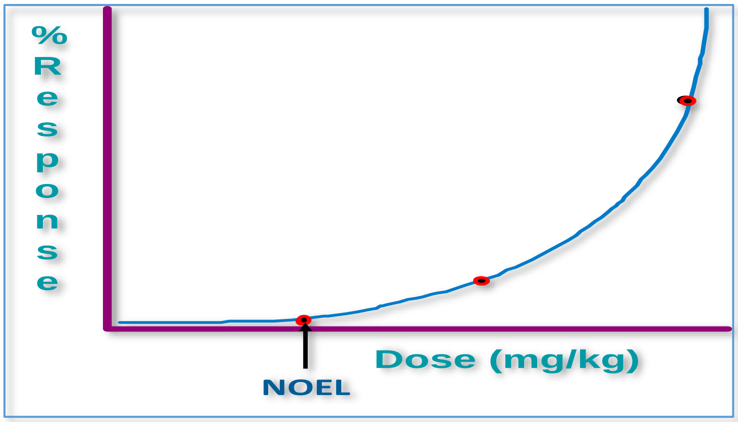


*Figure 4 : example of a dose/response curve*

Figure 4 shows and example of a dose/response curve. The response given on the Y-axis is the “effect” of the dose administered; the percentage of cases that showed an effect of the dose. In this example there is a point in the curve at which no effect is observed at all: the No Observed Effect Level or NOEL.

Dose/effect curves are very often non-linear and exponential type curves. Therefore they are commonly plotted on a logarithmic scale as shown in Figure 5.

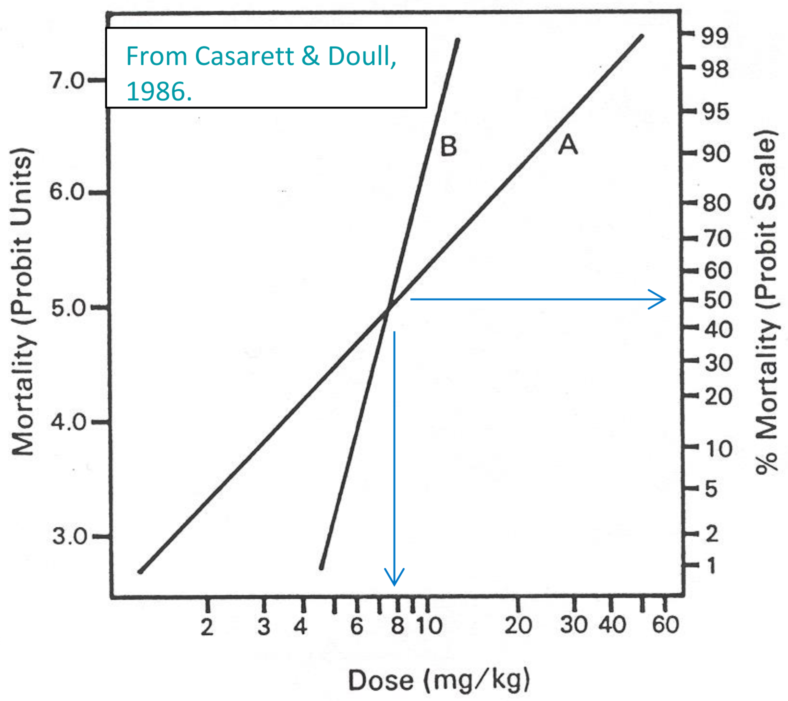


*Figure 5 Example of 2 dose / response curves on logarithmic scale*

As the curve is normally not linear it is not always straightforward to draw conclusions from only the LD50 value of a given substance or chemical.

To illustrate this shortcoming there are 2 dose/response curves drawn in Figure 5: one for chemical A and one for chemical B. They both happen to have the same LD50 value of 8 mg/kg but one cannot conclude that they therefore have equal toxicity.

To understand this consider a dose of 3 mg/kg: chemical A will cause mortality in the range of 5 – 10 % whereas chemical B causes no mortality at all. At low concentration the conclusion is therefore that chemical A is more dangerous than chemical B.

Now consider a dose of 20 mg/kg. Which of the two chemicals is “more dangerous” ?

Apart from the lethal dose or LD-values there are also some other values used in the toxicology:

- EDxx for example stands for effective dose, often used with medication
- TDxx stands for toxic dose; the dose that shows a toxic effect in XX % of the population

And sometimes all of these dose/response curves are determined for one particular chemical, for example for a medicine or vitamin. This is illustrated in Figure 6. The graphs shows the effective dose (bold black), the toxic dose (dotted) and the lethal dose (regular line) of a hypothetical vitamin. Drawing conclusions from it may become complicated.

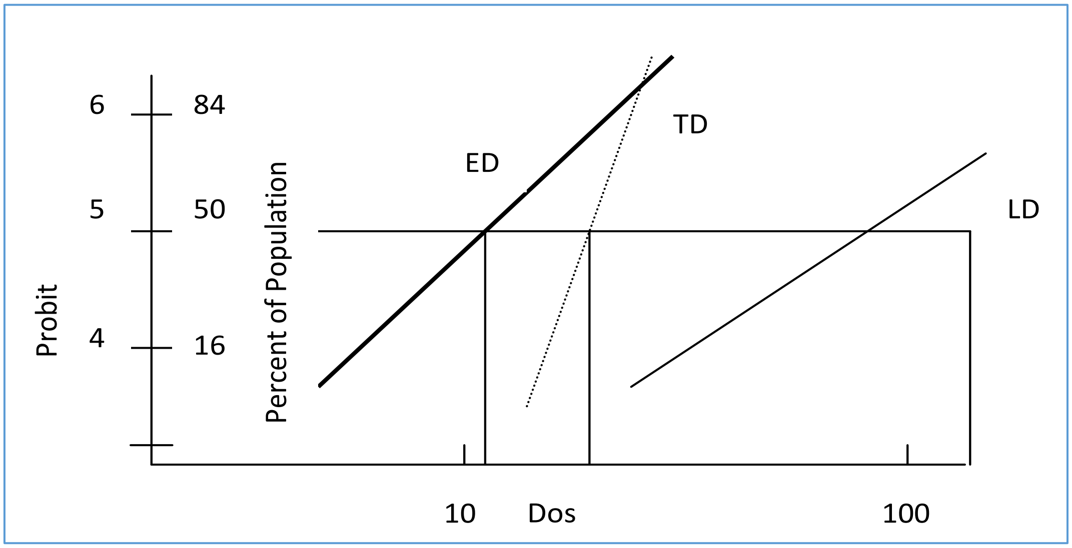


*Figure 6: ED/TD and LD dose response curves for a (hypothetical) vitamin*

Figure 6 shows one scenario for one substance in which the ED50 (depicted by the vertical intersection with the x-axis and representing the desired effect) is fairly close to the TD50 (depicted by its vertical intersection). In fact, the lowest lethal dose overlaps somewhat with the top effective dose. Also, the range of toxic doses is narrow. One might think of aspirin -- the effective dose can cause adverse effects in some individuals but its lethal dose is far higher than the effective dose and also higher than the toxic dose, depending on the toxic effect in question.

Looking back to Figure 4 one might think that there is always a no effect level that can be determined but that is not always the case. In toxicology there are two different methods used in dose/response relationships:

1. *threshold approach*: there is a dose below which no adverse effects occur in animals or humans, and
2. *non-threshold approach*: no matter how low the dose, there is always an adverse effect of some kind. The frequency of observed effects may be lower at lower doses but it will never be zero.

Threshold approach is typically assumed in Clinical observations, effects on Organ weight, Clinical chemistry and hematology, Developmental toxicity, Reproductive toxicity, Immunotoxicity, Neurotoxicity or Irritation effects.

Non-threshold approach is assumed when there is a probability of harm at all levels of exposure, for example when the chemical causes cancer, non-heritable mutations or heritable mutations.

To answer the question “What is a safe dose?” is therefore not straightforward; it will depend on the type of approach.

If a threshold approach is assumed then a safe dose is often defined as an Acceptable Daily Intake (ADI), or Reference dose (RfD), or Minimum Risk level (MRL), or Tolerable (daily) intake (TI or TDI), or Derived No effect level (DNEL).

In case of a non-threshold approach there is no dose without risk so the involved risk is part of the answer to the question what a safe dose is. Variations in doses are then also less important on short term. Then they use for example the LADD - lifetime average daily dose –to define safe levels.

Obviously the LD50 is hard to determine for a chemical that (only) causes cancer as every molecule one is exposed to give a CHANCE on developing a cancer…. But there may also be no effect at all! So how must one determine and compare toxicity of these chemicals? Toxicologists have defined a so called “potency” for that.

A potency is defined as the slope of the curve connecting the lowest estimated dose that causes a 10 % effect and zero, see Figure 7.

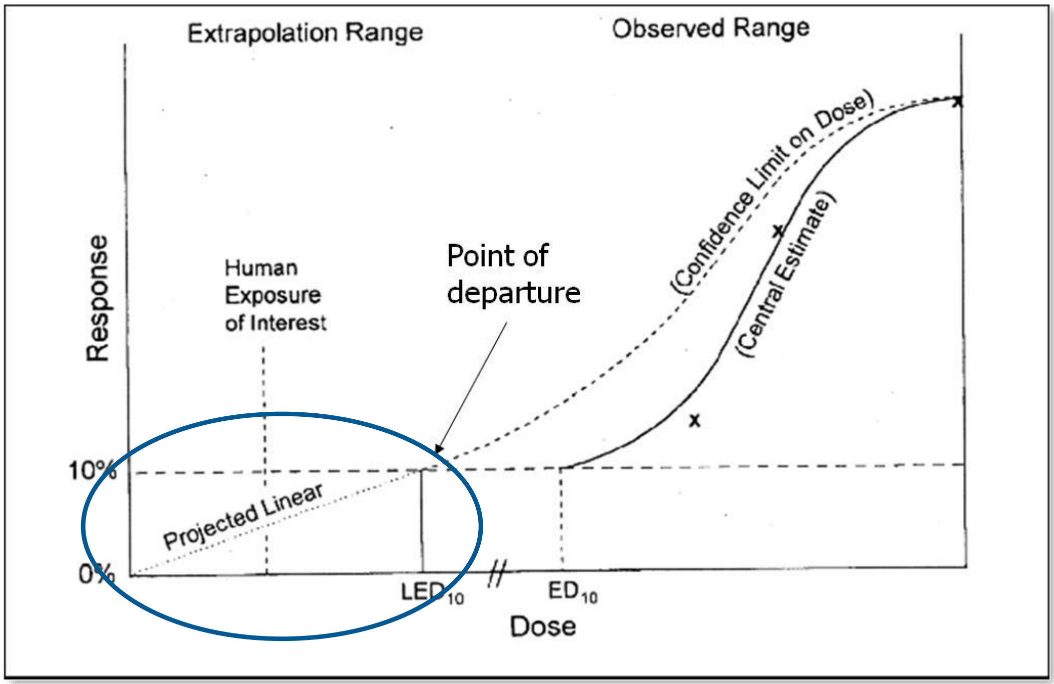


*Figure 7: how to derive a potency from LED10*

The measured dose/response curve is shown on the right; it’s the curve drawn through the 3 measured points (given by x); the central estimate curve. This calculated line however has a certain uncertainty as it is based on a few measured points only. With statistical methods you can define a confidence interval for the line and derive the low confidence limit for the ED10. This point is called the LED10 or the point of departure (PoD). To find the potency a line is drawn from the PoD to 0,0 and the slope of that line defines the potency. It has a unit inverse to a dose: (mg/kg-day)$^{-1}$

To illustrate the usage of a potency consider this example:

> A person is exposed over a period of time to chemical A. From the exposure data over time the calculated average daily dose (ADD) is established to be 0.04 mg per kg per day. The chemical is carcinogenic and is has been established that a dose of 5 mg/kg.day causes a 10 % response.
>
> Question1: what is the risk of the exposure to the chemical?
>
> Answer: the potency is calculated to be 0.1 (10%) / 5 (mg/kg.d) = 0.02 $(\text{mg/kg-day})^{-1}$.
>
> The risk involved equals potency times ADD = 0.04 * 0.02 = 0.0008 or 0.8 %
>
> Question 2: What is the acceptable (average) daily dose if we only accept a risk of 1 in a million (or less)?
>
> Answer: risk equals potency times exposure, so exposure equals risk divided by potency =
>
> 10-6 / 0.02 = 0.00005 mg/kg-day

Finding a dose/response curve is typically done by descriptive toxicologists. Obviously they do not conduct tests on humans. Instead tests have been developed in such way that conclusions can be drawn from tests on a variety of test animals. Administration of a variety of (relatively high) doses to a variety of laboratory animal species, should uncover all possible toxic effects while using the fewest numbers of animals in the tests. Tests on live organisms are called in vivo tests. Some tests can also be performed on samples of tissues in a laboratory setting. These are in vitro tests and are used for example to test skin irritations or - sensitization.

There are 3 levels of toxicity tests:

*Level 1: Acute effects* these tests are designed to determine effect upon direct contact to the substance or a single exposure. They may serve as an early screening and are valuable as they give information needed in cases of (single) accidental exposure. The program involves determination of acute LD50 values for oral, dermal and inhalation exposure as well as eye and skin irritation and sensitization (allergy testing). The acute test program also has a mutagenicity screening, often performed in vitro.

*Level 2: Sub-Chronic effects* the tests in this program are aimed at the type of toxicity produced (effect on targeted organs) and finding at what relative dose effects occur. The outcome of these tests is needed to determine safe values for a workplace “standard” such as a TLV (threshold limit value). These tests are more widely used, especially with new chemistry or new molecules. The program involves 90-day to 1-year studies for the likely exposure routes and looks at additional mutagenicity, reproduction toxicity, immunotoxicity and neurotoxicity. Usually the metabolism / mechanism is studied in the test animals so that adequate translation can be made to human physiology.

*Level 3: Chronic effects* these tests are aimed to find chronic effects and are used to determine cancer potential for example. Results of chronic tests are also needed for establishing allowable food concentrations, to further examine suspicious activity seen in earlier, shorter tests. Also epidemiology studies are typically trying to establish chronic effects of exposure to chemicals. The program involves lifetime studies in rodents (mice / rats) and could take several years to complete.

In order to assess the hazard of chemicals normally several tests are conducted to assess these properties. For classification and labeling purposes these tests have been standardized and have predefined criteria. Tests are done to determine:

- Acute toxicity
- Skin corrosion/irritation
- Serious eye damage/eye irritation
- Respiratory or skin sensitization
- Germ cell mutagenicity
- Carcinogenicity
- Reproductive toxicity
- Specific target organ toxicity in case of single exposure
- Specific target organ toxicity in case of repeated exposure
- Aspiration hazard
- Hazard / toxicity to the aquatic environment
- Hazardous effects to the ozone layer

## 3.3 Exposure

Back again to Paracelsus: “the dose makes the poison”. The previous chapter has described the possible effects on the human body and how to properly assess them. In this chapter we look more closely on the exposure side.

The primary question in exposure assessment is: “How and how much (of the chemical) has entered the body?”

Chemicals can enter the body via three different routes: through the lungs (inhalation), through the digestive system (swallowing) and through the skin. Factors that are critical to exposure are the duration of the contact, the route, the bioavailability of the substance and the concentration in the media.

*Digestive system.* When chemicals are swallowed they can be taken into the body on several points but in general they have to cross a barrier like the wall of the gut. Oral exposure is likely to occur in industrial situations (workers in plants for example) as it is relatively easy to avoid this type of exposure; if eating and drinking is not allowed in process areas the likelihood of oral exposure is minimal. Some chemicals are even less toxic when swallowed compared to other routes of exposure. This is due to the fact that in case of inhalation and/or skin absorption the chemical will enter the bloodstream more easily. As example: mercury is less harmful swallowed than if inhaled as vapor.

*Inhalation.* Vapors, gases, mists and aerosols may enter the body through inhalation and subsequent absorption in the alveoli. Especially for volatile lipophilic substances like benzene or aliphatic chloro-hydrocarbons are easily absorbed in the alveoli and enter the bloodstream like that. Once in the blood they pose a threat to the brain tissue that itself is very lipid.

Not all gases are easily absorbed in the alveoli; water soluble gases like HCl, $NH_3$ and $SO_2$ are dissolved into the watery slime layers in nose and throat and absorbed there or swallowed as solution.

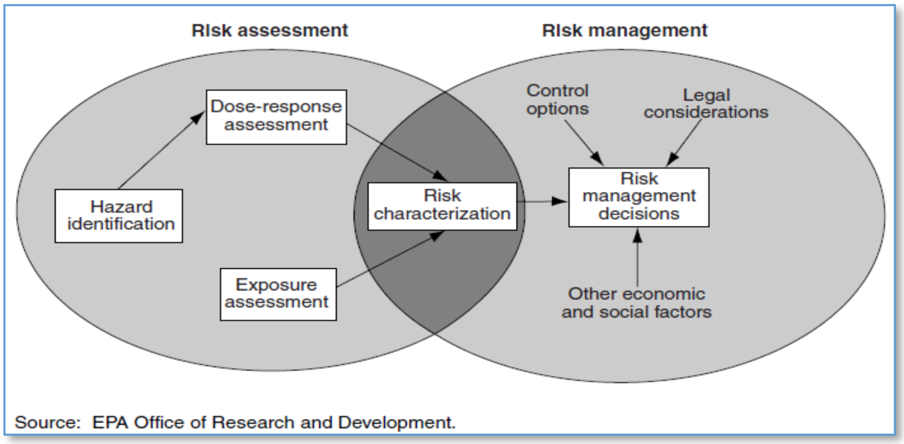
It is easy to understand that the air quality in work places close to chemical plants has a big impact on the safety of the people working there.

*Skin.* The skin is in general a good barrier against incoming substances. First of all it consists of 2 layers: the outer layer – the epidermis – and below that the second layer – the dermis. At places where hairs are the epidermis is bulged inward and has sebaceous glands. The tallow layer is difficult to penetrate for hydrophilic substances. Lipophilic substances however penetrate the layers relatively easy. The presence of local sweat also influences the ability of penetration of substances. Gases normally do not penetrate the skin. The exception to that rule is hydrogen cyanide (HCN) and working with that gas not only requires a gas mask but also good skin protection to avoid toxic effects.

The skin as protection layer needs to be protected in order to work properly. If the tallow is washed off with organic solvents then the penetration of dangerous substances is bigger. Same applies to washing with an abrasive cleaning agent may damage the epidermis and opens the door for penetration of the skin.

## 3.4 Toxic Risk Assessment and Risk Management.

The assessment of the risk imposed by coming into contact with chemicals needs knowledge of the toxicity of the chemical and the exposure to that chemical, in other words: dose/response assessment and exposure assessment. With these two elements the risk can be characterized/assessed.



Source: EPA Office of Research and Development.

*Figure 8 Typical Sequence of Risk Assessment and Risk Management Processes*

The next step is to control or reduce the risk to an acceptable level. That is called Risk Management. Risk management decisions are influenced by many factors such as legal considerations, possible control options and other economic and social factors, see Figure 8.

Legal considerations can be maximum exposure limits set by regulation, control option may be personal protective equipment or engineered solutions (ventilation for example in controlling an inhalation risk), economic factors may be the cost of alternative technology and social factors are for example the generally accepted risks by groups or cultures.

When the hazard of the chemical is properly assessed, the exposure quantified and controlled and management systems and methods installed to mitigate inacceptable risk we can state that the situation “is safe”; the residual risk is acceptable.

# 4. Fire & Explosion

## 4.1 Flammability and Fire

Fire in principle is an (usually) unwanted and uncontrolled form of oxidation. The consequences of a fire can be devastating and due to the uncontrolled nature they pose a significant threat when a fire breaks out in a chemical plant. In ancient times a fire was considered a force of nature, similar to a flood or lightning. Nowadays we have a lot of knowledge on the processes behind a fire which allow it to be controlled… usually. Plans always have to assume that a fire gets out of control.

An oxidation is a reaction of a flammable substance with oxygen present in the air. For example a fire of methane gas has the following reaction scheme:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{energy}$$

The released energy manifests itself as heat (-radiation) and for a small part as light: the light of the flame.

A fire of methane does not start by itself when the methane is mixed with oxygen and/or air, so something else is needed to create a fire. This third ingredient is an amount of energy. This initial energy bumps the reaction past the activation energy of the reaction after which the reaction itself provides further heat to sustain the oxidation. We call the activation energy the ignition energy.

Ignition energy can be given by a flame, a spark, by friction or by other means but whether or not an ignition source will start the fire also depends on the flammable material: different substances have a different minimum ignition energy. The property used to define the sensitivity of the chemical to ignition is called the

- *Minimum Ignition Energy (MIE)* – minimum amount of energy required to ignite a combustible vapor, gas or dust cloud.

However, not always does one need an ignition source to create a fire. If the temperature is sufficiently high the chemical may spontaneously overcome the activation energy of the reaction and ignite. This point of auto-ignition is also a property of the chemical and is called the

- *Auto Ignition Temperature (AIT)* – lowest temperature at which a material will spontaneously ignite and continue burning in a normal atmosphere.

In summary we need three ingredients for a fire: a flammable material (fuel), oxygen and an ignition source as depicted in Figure 9.

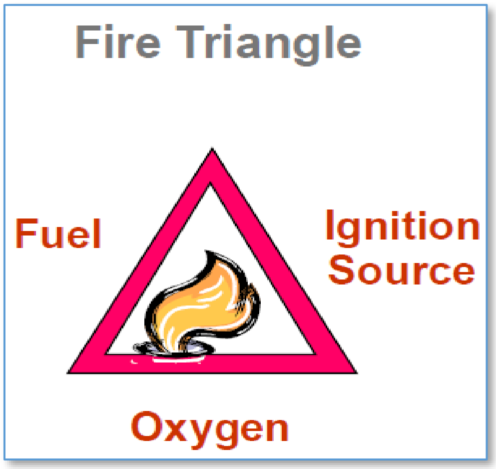


*Figure 9 : Fire Triangle*

Take one of them out and the fire dies. This is the essence of fire extinguishing equipment; they eliminate one of the three sides of the fire triangle, for example

- A fire blanket for example removes access to the surrounding air thus taking out the oxygen.
- Fire water from sprinklers lower the temperature of the reacting mixture because water can absorb considerable amounts of heat and thus lowering the reaction temperature until the fire can no longer sustain itself.
- $CO_2$ extinguishers combine the temperature reduction effect with replacing the air in and close around the fire with inert molecules.
- Etc.

The combustion reaction of a fire nearly always generates more gas molecules after reaction than there were before it; usually 6 – 8 times more moles than the starting materials.

Gases, liquids and solids of flammable materials do not have the same burning properties and so extinguishing gas fires for example needs a different approach than extinguishing a burning liquid.

### 4.1.1 Flammability of Gases.

Gases are the easiest form to burn and always have a flame when burning. Reason for that is that gases easily mix with air which allows for a homogeneous reaction. The reaction however cannot run if the mixture or fuel and air is too far away from the stoichiometric rate: too little fuel present will stop the reaction as well as too much fuel. Gases therefore have two flammability limits:

- *Lower Flammability Limit (LFL)* – lowest concentration of a substance in air that will sustain combustion, and
- *Upper Flammability Limit (UFL)* – highest concentration of a substance in air that will sustain combustion.

As oxidation reaction with gases may run explosively these limits are also called lower / upper explosion limits and the commonly used unit for them is %-vol (in air).

When the reaction takes place in a gas-mixture containing more or less air than air these limits will change. Decreasing the oxygen will make it harder to sustain the reaction and there is therefore a point below which the fire can no longer propagate a flame. It is called the

- *Limiting Oxygen Concentration (LOC).*

Increasing the oxygen to ultimately 100% oxygen in the air mixture will not limit the reaction but instead will widen the spread between LFL and UFL compared to the values in air.

Most organic substances have a limiting oxygen concentration of roughly 9 to 10 %-vol if nitrogen is the inerting gas. A “non-ignitable” atmosphere is commonly defined at less than 5 %-vol oxygen (roughly half the LOC). Notable exceptions to the rule of 9-10%-vol for organic compounds are Acetylene, Carbon Disulfide, Carbon Monoxide, Ethylene Oxide, Propylene oxide and Hydrogen. All these substances have a considerably lower LOC.

How the air value of LFL and UFL relate to the concentration of oxygen and fuel in a ternary mixture of an inert (nitrogen), oxygen and fuel is depicted in Figure 10.

With this diagram one can estimate the flammability limits in all situations of concentrations of oxygen in the vapor space.

It is also clear from this figure that if the oxygen concentration is kept below the LOC the mixture of fuel vapor and (low O2-) air is no longer a fire or explosion hazard, hence “safe”. This techniques is more commonly known as inerting the gas phase and is very commonly used in storage tanks containing flammable liquids to avoid the development of a flammable mixture in the vapor space.

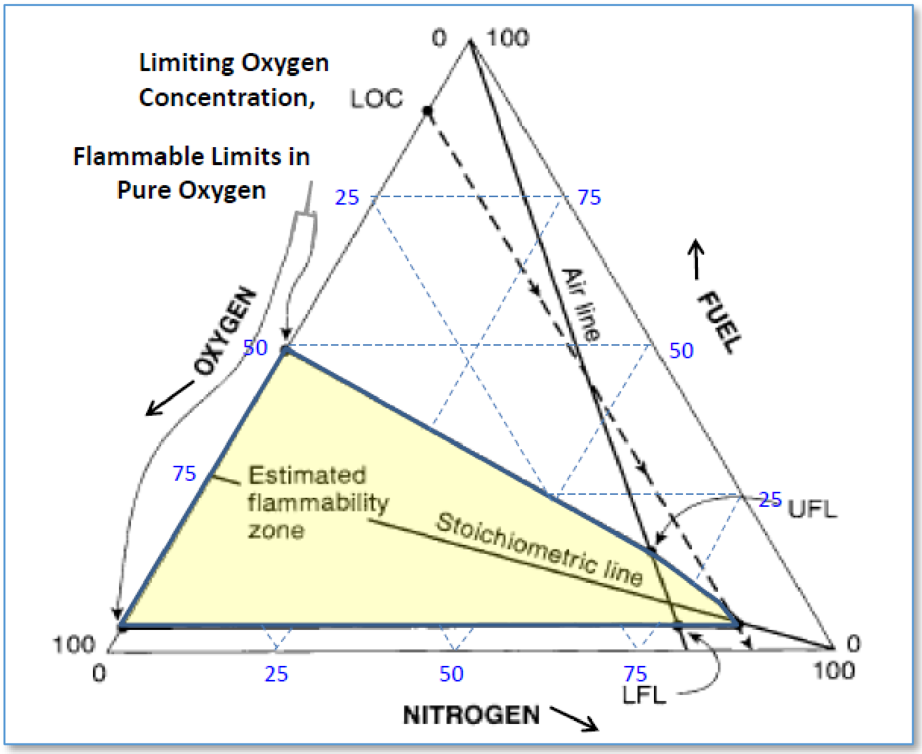


Figure 10: flammability (ternary) diagram

Mixtures are very common in chemical processing. The Lower Flammable Limit (LFL) for mixtures may often be estimated from Le Chatelier's equation:

$$\mathbf{LFL_{mix} = 1 / \Sigma ( y_i / LFL_i )}$$

Where $y_i$ the vapor mol fraction and $LFL_i$ the Lower Flammable Limit for each component i.

### 4.1.2 Flammability of Liquids

Liquids do not burn. The oxygen concentration in the liquid is too low to sustain the reaction. However, when energy is added to the liquid and it vaporizes then the vapor can ignite and burn, in turn providing the heat necessary to evaporate the fuel for the flame. The flammability of liquids is therefore more defined by the evaporation rate of the liquid. Highly volatile flammable materials will pose a bigger flammability risk than low volatility liquids. If enough molecules are vaporized to create a flammable gas/air mixture then this mixture can be ignited and a flame results.

The governing property to define the flammability of a liquid is called the

- *Flashpoint (FP)*: the lowest temperature at which a liquid will give off sufficient vapor to be ignited in air.

It may be estimated as the temperature at which the equilibrium vapor composition in air is approximately equal to the lower flammability limit of the corresponding gas phase.

There are 2 method for measuring the flashpoint: with an open cup or with a closed cup. The resulting flashpoint temperature of the same chemical measured with these two methods will differ as the open cup has a different impact on the evaporation of the liquid.

The flashpoint of a liquid is dependent on the conditions at which it is measured; the atmospheric pressure and the concentration for example play a big role. This is illustrated by the following observations:

The flashpoint of toluene measured in Breda (at +10 m NAP) has been measured to be 4 °C. However, the same toluene measured in Calgary (at +1700 m NAP) is measured to be 1 °C

The flashpoint of pure ethanol is 12 °C. But the flashpoint of cognac is much higher: 25 °C. And beer has an even higher flashpoint: > 90 °C

### 4.1.3 Flammability of solids

In case of solids there are three situations:

- Direct burning of a solid or glow fire: a number of chemicals can react directly with oxygen at the surface of the material. The substance will radiate light, or glow. Examples are wood in a fireplace, charcoal in the same situation and glowing metals. The fire is not very spectacular because of the lack of flames but can reach very high temperatures which makes is very dangerous. These fires require a special extinguishing technique.

- Fire after melting and vaporizing: the chemical melts and then vaporizes and the vapor burns with a flame. The classic example is a candle: solid stearin melts close to the flame and the liquid is sucked up by the cotton fuse. There it vaporizes and fuels the flame.
- As result of Pyrolysis: most solid substances will not melt by heat of a fire but will instead decompose which is called pyrolysis. With the pyrolysis gases and liquids may be formed that (evaporate in case of liquids and subsequently) ignite in the fire.

## 4.2 Explosions

An explosion can be defined as a

> *(very) rapid release of a large amount of energy resulting in a rapid pressure build-up.*

In other words: a “BOOM”.

The energy released can be in form of heat, fragments with large impulse, blast wave, etc.

The dangers of explosions are many; there is

- a pressure-wave or shock-wave
- sometimes fire; a fireball or flashfire
- sometimes debris flying around at high speeds
- sometimes vibrations in the ground (a ground shock)
- sometimes a large wave or tsunami when big water surfaces are present
- sometimes releases of poisonous gases or asphyxiates
- sometimes collapsing building or structures

… and they all can cause significant hazards for people in the area.

There are two principle different pressure effects of explosions: a pressure wave or a shock wave, see also Figure 11

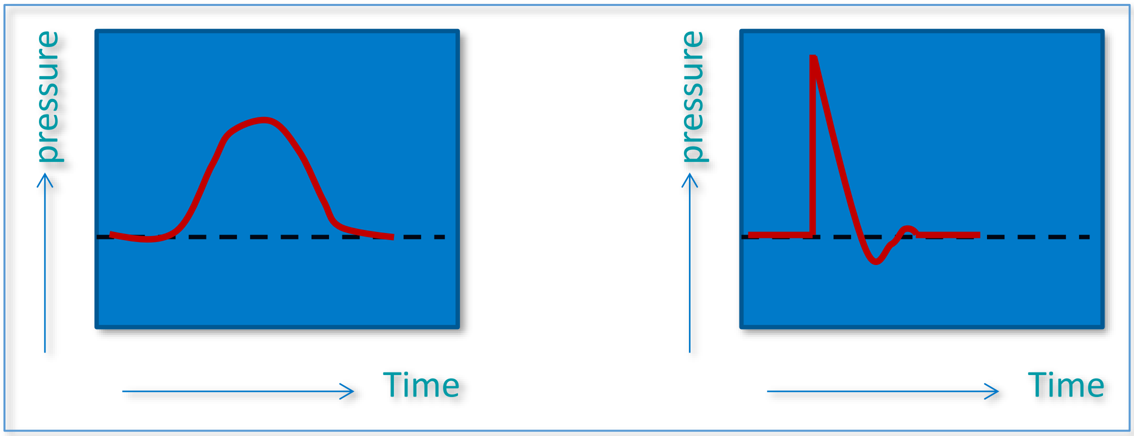


*Figure 11: pressure development in a pressure wave or a shock wave*

A pressure wave has a relatively slow rise time and feels like wind. This type is often seen with gas- or dust explosions.

A shock wave has a rise time of almost zero and a very rapid pressure relief. After the relief there is some under pressure notable as well. This type is seen with detonations and does not feel like a wind but like a BOOM.

The peak pressure of the pressure wave is a measure for the destructive force of an explosion but the actual peak pressure does not even have to be very high to cause damage. See also Figure 12.

Source: Handboek Gevaarlijke Stoffen ( 1 kPa = 0.01 bar)

| Damage | Peakpressure/ kPa |
|---|---|
| Damage to glass panels | 0.1 – 0.3 |
| Broken windows, rupture of plaster, minor damage to buildings | 3.7 – 7.5 |
| People knocked over | 7 – 10 |
| Walls made of concrete blocks collapse | 12.5 – 20 |
| Oiltanks rip open | 20 – 30 |
| Serious damage to buildings made with a steel frame | 30 – 50 |
| Trains knocked over | 40 – 60 |
| Total destruction of reinforced concrete buildings | 70 – 80 |
| Deadly destruction | 700 - 150 |

*Figure 12: peak-pressure effects of explosions*

Flammable vapor reactions with oxygen can cause fires but can also cause explosions. Fires and explosions as result of oxygen reactions have therefore a lot of similarities. They both require the presence of a fuel, oxygen and an ignition source. However there is a difference too, as shown in Figure 13.

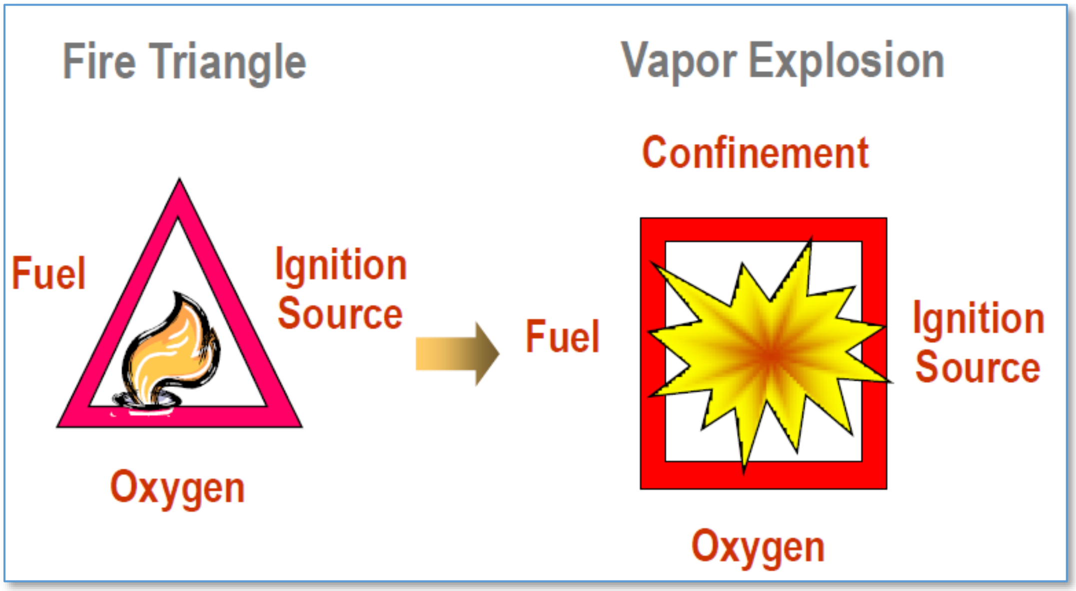


*Figure 13: Vapor Explosion Rectangle.*

In order to create an explosion with a cloud of flammable vapor a forth element is needed: confinement. Igniting a flammable vapor cloud in open space will “only” create a puff as the oxidation reaction takes place. However, if the same is done in a confined space the pressure buildup magnitudes bigger and causes an explosion.

In simple terms: a fire is an oxidation with air in a constant (atmospheric) pressure situation whereas an explosion is the same in a constant volume situation.

There are many types of explosions that can be grouped as shown in Figure 14.

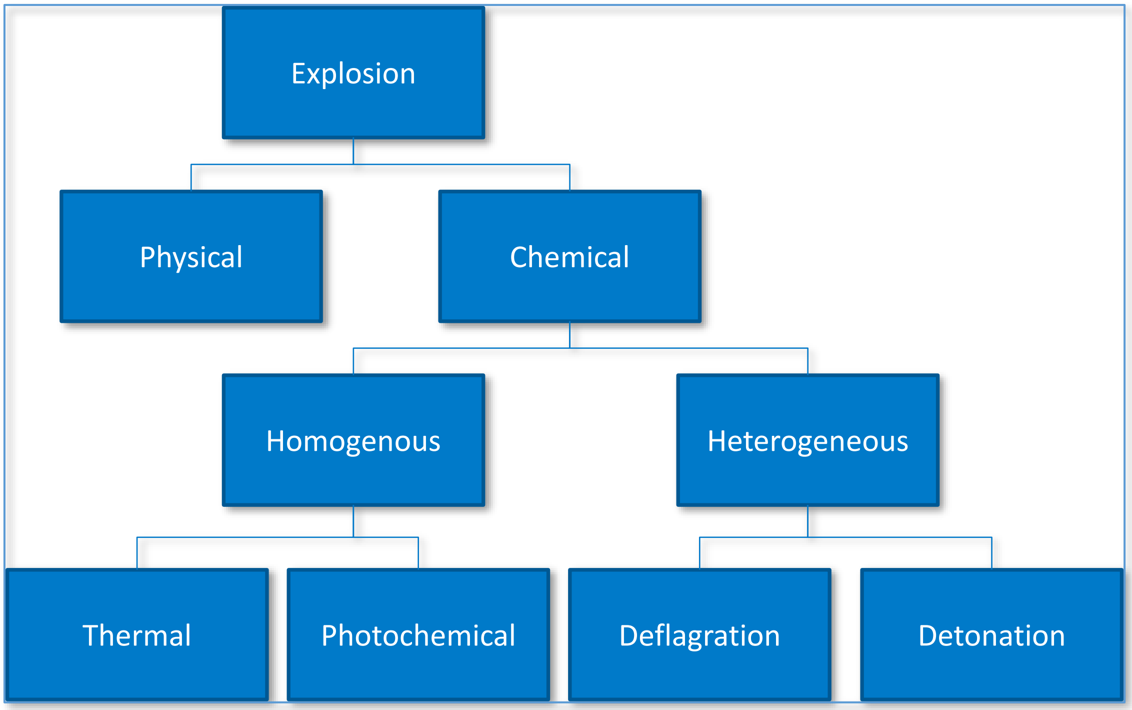


*Figure 14: Types of Explosions*

### 4.2.1 Physical Explosions

Physical explosions differ from chemical explosions by the fact that they do not have a chemical reaction ongoing. There is a rapid energy release but not due to an ongoing chemical reaction. Examples of such explosions are the rupture of a pressurized vessel, the lightning striking, a nuclear explosion, a volcano erupting or a so called BLEVE.

A BLEVE is a Boiling Liquid Expanding Vapor Explosion and is special in its mechanism. The actual explosion is caused by an external fire at a liquid filled tank, however the fire – a chemical reaction – is not the direct cause / reason for the explosion. What happens is this:

- starting point is a tank with flammable liquid that is protected with a safety valve against overpressure
- an external fire heats up (part of) the tank causing the liquid to heat up inside the tank.
- The pressure in the tank rises and the liquid starts to boil as result of the heat input. The safety valve on the tank opens to relief the overpressure.

So far no harm is done and the safety valve is actually protecting the tank against an explosion due to overpressure in the tank. But then the situation goes on:

- The boiling process inside the tank causes the liquid level in the tank to drop. However, the liquid in the tank was actually the protection of the tank metal wall as it absorbs the heat from the fire. All parts of the wall that are in contact with the liquid level inside the tank stay cool, but the wall metal in contact with the vapor space is not cooled adequately.

- The liquid level drops to a point that parts of the tank wall metal heated up by the fire are no longer cooled and start to weaken. At a certain point it gives in to the pressure inside the tank causing a large release of vapor and liquid directly into the external fire which ignites it and a massive explosions results: the BLEVE.

### 4.2.2 Chemical Explosions

As said chemical explosion involve a chemical reaction. During the explosion the reaction energy is always released and new components formed. Once the reaction has started it will go on with or without supply of energy (or matter). As with all chemical reactions there is a common pattern in the development of the energy, see Figure 15.

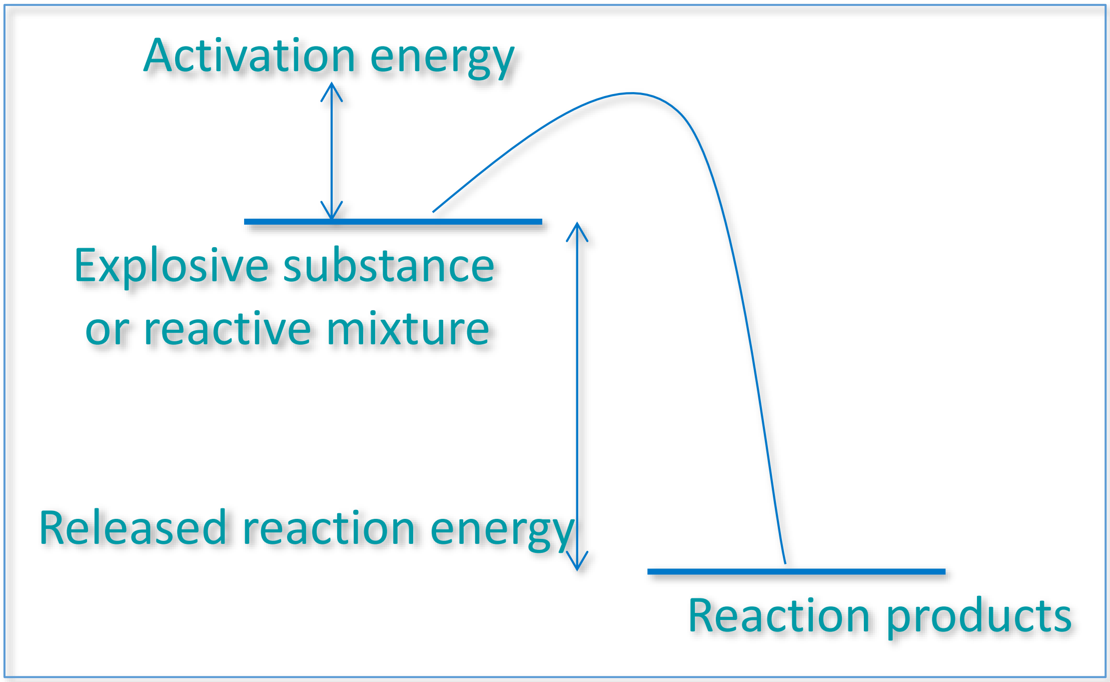


*Figure 15: Energy development of energy in chemical explosions*

There are 2 types of chemical explosions: homogeneous explosions and heterogeneous explosions.

#### *4.2.2.1 Homogeneous chemical explosions*

In case of homogeneous explosions the reaction is taking place at all places / everywhere at the same time. The entire mass reacts at the same time, often triggered by electromagnetic radiation (light) or heat. Examples are the reaction inside a diesel engine, a decomposition reaction causing an explosion (nitroglycerine decomposition for example) or compression of hydrogen / oxygen mixtures.

True homogeneous explosions require special conditions to occur. In case of a diesel engine there is a rapid (adiabatic) compression of the mixture causing the combustion reaction to occur everywhere in the cylinder at the same time. No ignition source is needed for the explosion in contrast to petrol engines which require a spark to ignite the mixture.

The type of ignition will determine the type of homogeneous explosion: it's either a thermal explosion or a photochemical explosion.

Homogeneous explosions do not (or at least hardly ever) occur in solid materials as in those cases there is always a reaction-front present.

Exothermic reactions that take place in a situation where the heat generated exceeds the heat removed can cause a so called runaway reaction, in turn leading to a thermal explosion. The reaction generates more heat than can be removed and as a result the temperature rises. This in turn increases the reaction rate of the reaction thus increasing the heat production even further etc. etc.

As the heat production increase of a reaction usually follows an (exponential) Arrhenius curve when the temperature rises but heat removal (by transport) usually increases linearly with increasing temperature it is easy to understand that at a certain point things can no longer be controlled anymore. With runaway reactions there are three regions in time that allow for different actions to counter the ongoing reaction before it develops into a catastrophic event, see Figure 16.

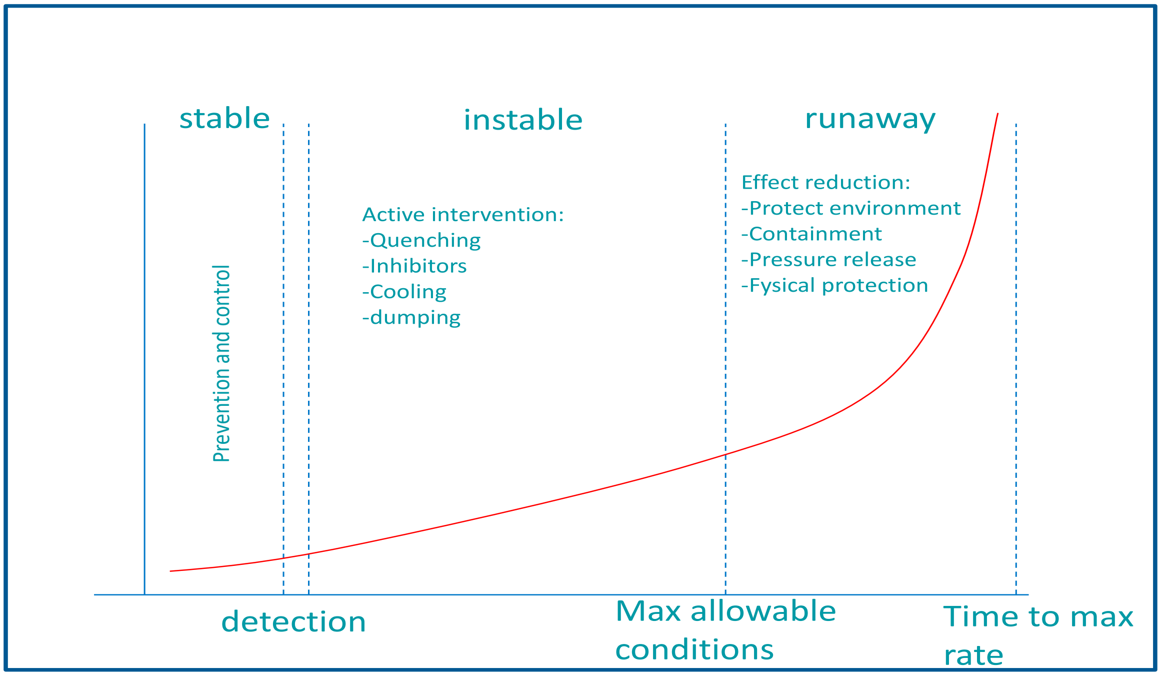


*Figure 16: Runaway reaction*

In the stable zone there is little activity and normal operations are taking place. System with potential runaway reaction however usually have a detection system to detect that the reaction has started; for example a temperature measurement triggering an alarm when a certain set-point is exceeded.

In the instable zone there is a situation in which the results of the ongoing reaction can be controlled. Interventions that may prevent an explosion may be quenching of the system with cold, non-reacting material, external cooling, inhibitor addition, or dumping of the content in a safe location. The interventions are aimed at removing the produced heat and/or stopping the reaction.

If interventions are not successful the reaction reaches the maximum allowable conditions after which a runaway reaction is unavoidable. The only measure left to be taken are effect reductions such as protection of the surroundings, explosion containment (if possible at all), pressure release from the system and physical protection. Based on the curve that the temperature increase follows one can predict the time to maximum rate aka the explosion. If all interventions fail then people have to be brought to safety before this point is reached.

#### *4.2.2.2 Heterogeneous chemical explosions*

In case of a heterogeneous explosions the reaction is triggered in one place and then runs through the material. In principle one could distinguish 3 zones in the material: the original materials, the reaction zone and the decomposition zone. The actual reaction takes place in the reaction zone only whereas the reaction products form the decomposition zone and the original material in the unreacted zone gets consumed.

Almost all unwanted explosions are heterogeneous; the reaction starts for example by friction, a bump, a flame, and then runs through the material. The next layer of material comes to reaction by a change in conditions: it can be heated up by the reaction zone or it can be adiabatically compressed by the reaction zone.

If the energy transfer from reaction to unreacted material is heat transfer then we call this type of explosion an explosive oxidation or deflagration. Speeds of the reaction front are in the range of $10^{-5}$ to 5 m/s. The corresponding pressure wave has the form of a wave as shown in Figure 11.

In cases where the energy from the reaction zone is transferred by pressure (expansion of the reaction zone causes an adiabatic compression of the unreacted zone) we call the explosion a detonation. The speed of the reaction zone and the subsequent pressure wave are much higher compared to a deflagration; $10^3$ to $10^4$ m/s , well above the speed of sound! The shockwave is supersonic and hits instantaneously as shown in Figure 11.

### 4.2.3 Dust explosions

A dust explosion is a chemical explosion of a flammable mixture of powder with oxidant (usually air).

It is therefore by definition also a heterogeneous explosion as the reaction takes place at the surface of the material. Thinking about it some more it becomes clear that next to the four elements needed for an explosion also a fifth one comes into play: creating a mixture of the material with the oxidant. Solids are more subject to gravity and will settle if "thrown into the air". Once settled there is no longer a flammable mixture of reactant with oxidant.

So apart from a flammable material (fuel), oxygen (air), confinement (constant volume) one needs also a suspension in the air or aeration, see Figure 17.

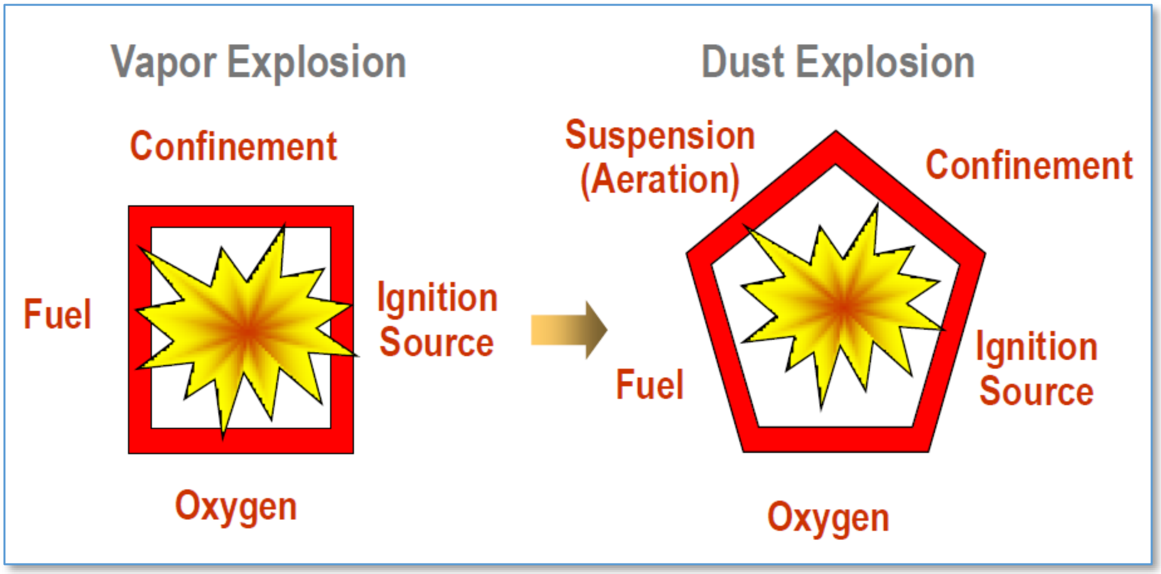


*Figure 17: Dust explosion Pentagon*

The resulting explosion will be a deflagration and not a detonation as compression of the unreacted material by the reaction zone hardly plays a role in the reaction. The transfer mechanism is therefore always heat transfer.

A dust that can cause a dust explosion is called a combustible dust as is defined as

> A finely divided solid material, 420 microns or smaller in diameter (500 micron for some EU regulations) which present a fire or explosion hazard when dispersed and ignited in air.

The particle size of the material plays a key role because of the surface to volume ratio: the bigger the particle the smaller the surface/volume ratio. High surface areas create a bigger reaction zone and hence produce more heat of reaction per unit of time. At the same time it is easier for smaller particles to be suspended in air which adds to the hazard.

The concentration of dust particles in the air is not as critical as the stoichiometric composition is to gases in order to explode. Combustible dusts can explode in the range of 20 – 6000 g/m$^3$

A rule of thumb often used is this

> A dust cloud is explosive when you cannot see your hand on a stretched arm anymore in the cloud.

Dust layers of combustible dusts are known to be hazardous at a thickness of 0.2 > 0.5 mm. The hazard from situations with this thick layers of dust present is not that they can be ignited as such. After all they are not suspended in air (yet). The true danger results from what is known as the secondary dust explosion.

A secondary dust explosion occurs after the primary explosion and is usually much stronger. The first explosion's pressure wave releases all layers of dust into the air creating the needed suspension and carrying with it the ignition source: another dust explosion is unavoidable.

## 4.3 Ignition.

Even though most reactions involving fire and explosions are running on their own they normally do not start by themselves. A certain amount of energy – the ignition energy - needs to be added. This also applies to spontaneous reactions. Looking at Figure 15 that makes sense and it is also understandable that the ignition energy needed will depend on the reaction, hence on the starting material. Typical observed minimum ignition energies are:

Organic chemicals: 1 – 10 mJ

Natural products: > 10 mJ

Soot: > 4000 mJ

Hydrogen: 0.012 mJ

Propane: 0.21 mJ

The value depends on the temperature, concentration etc.

The minimum ignition energy for a combustible dust mainly depends on the particle size as shown in Figure 18

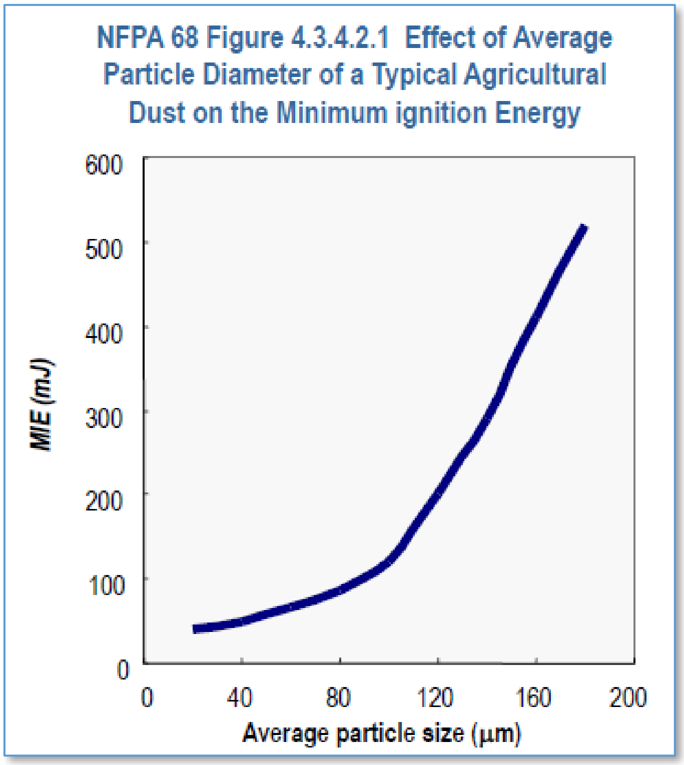


*Figure 18 Effect of avg. particle size on MIE for a typical agricultiral dust*

There are many ways to ignite a flammable mixture. To name a few:

- *Process related ignition sources:* static electricity, hot surfaces, hot gases, flames, Chemical reaction, smoldering, fired heaters or boilers, etc.
- *Equipment related ignition sources*: Electrical -, radiating equipment, etc.
- *Activity related ignition sources:* Welding, cutting sparks, friction heat, etc.
- *Other sources:* combustion engine, Lightning / thunder storms, radiation, sun, etc.

Adiabatic compression can also act as an ignition source. Heat from compression may result in a temperature which exceeds the Auto Ignition Temperature for a flammable mixture, resulting in ignition. The temperature after adiabatic compression can be calculated with

$$T_f = T_0 (P_f / P_0)^{(\gamma-1)/\gamma}$$

Where $T_0$ and $P_0$ are the initial absolute temperature and pressure (note that $\gamma$for air is 1.4 such that he exponent above is roughly 0.29)

Finally there is ignition without an ignition source: auto ignition.

The auto ignition temperature of many chemicals have been determined and collected and can be found in handbooks and Material Safety Datasheets. Some examples are:

- White Phosphorus: 34°C
- Sodium: 25°C
- Frying oil: 370°C
- N-Octane: 210°C
- Hydrogen: 560°C

Hydrogen in this list is interesting as it is extremely flammable with very low MIE and, being a gas, very easily forms explosive mixtures. But in pure form it is quite hard to ignite it; a temperature of well above 500 °C is needed.

Based on the auto-ignition temperature of the chemical there is a classification for equipment into 5 different groups, see Figure 19

| Group | Max. surface temp.°C | AIT of substance °C |
|---|---|---|
| T1 | 450 | ➢450 |
| T2 | 300 | 300 – 450 |
| T3 | 200 | 200 – 300 |
| T4 | 135 | 135 – 200 |
| T5 | 100 | 100 – 135 |
| T6 | 85 | 85 – 100 |

*Figure 19 Temperature groups for equipment based on AIT of substance*

# 5. Full Scale production of chemicals

## 5.1 Process Safety

Full scale production of chemical products requires a different approach than production of the same products on small or laboratory scale even though the same chemistry is applied. This is best illustrated with an example:

Suppose a chemical product can be purified using a vacuum distillation.

In a laboratory set-up this will require a flask suited for vacuum, a condenser, a vacuum pump, a jacket-heater, a distillate collector and some measurement equipment (thermometer, pressure measurement as a minimum).

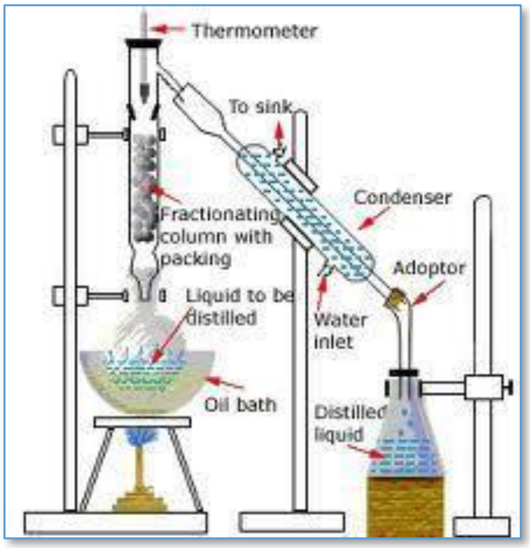


*Figure 20: laboratory set-up for distillation*

Looking at this set-up with process safety eyes we can recognize these potential hazards:

- Filling the flask with the starting material there is a risk of spilling it on the lab. Bench or even in the heater which in turn can cause a fire when the heater starts heating.
- Reassembly of the (glass) system may have some errors potentially causing a glass failure when the vacuum is applied to the system.
- The cooling medium (often water, but may also be more hazardous materials) is not turned on in time and as result the condensate is not condensed and hot gases enter the vacuum unit with unpredictable effects.
- The pressure measurement is malfunctioning and as result the pressure is a lot lower than the glass can handle causing an implosion or causing a situation with vacuum still on the system while it is opened for collection of the distillate in turn causing a glass failure hazard

- The temperature measurement is malfunctioning causing the heater to provide much more heat to the system than expected causing unpredictable results such as runaway reactions, by reactions, overloading of the condenser, coke formation, etc.
- The heater is malfunctioning with similar effects.
- The vacuum-unit is not turned off and the pressure leveled to normal before opening the system to collect the product causing a failure of the glass system and subsequent cutting hazards.

And there may be more hazardous situations who have not been identified in the above list.

In a full scale production set-up the same vacuum distillation will, most likely, be carried out in a continuous vacuum distillation column.

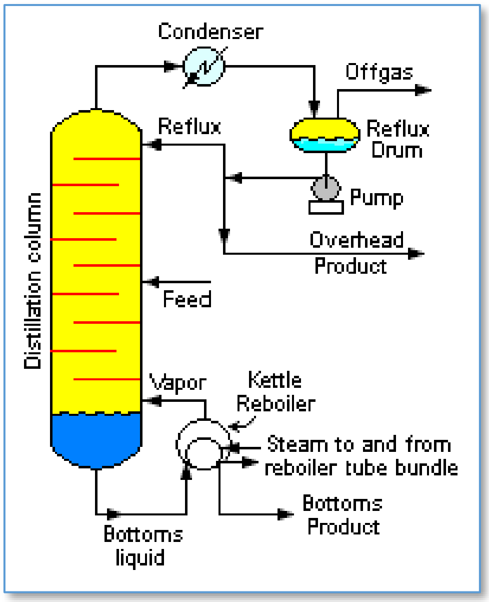


*Figure 21: schematic for continuous plant distillation*

The list of required pieces of equipment in this case is a lot longer: distillation column with trays or packing, a reboiler, a reboiler pump, a heating medium supply system for the reboiler (hot oil or steam, or..), a feed pump, a cooler / condenser, a reflux pump, a vacuum pump, storage tanks for feed as well as the two products, several process measurements such as pressure transmitters, temperature transmitters, flow measurements, automated block valves that shut off flows in case of emergencies, pressure safety valves and vacuum relief valves to protect against damage by over- or under pressure, emergency switches, a control system controlling the process, …

It is therefore obvious that the list of things that might go wrong and/or pose a hazard is also a lot longer. To study those scenario’s and risks involved all kinds of tools and methods have been developed by process safety risk experts.

But the basic rules of good process safety are actually very simple:

- Rule #1: whatever is inside of the equipment needs to stay inside, and
- Rule #2: whatever is outside of the equipment needs to stay outside.

In other words: the process needs to be protected against opening up and releasing the content or taking in anything from the environment around it.

However, sometimes we want the process to be opened up. Examples of intentional process equipment openings are: taking a sample, connecting a hose for loading or unloading, opening hatches to add material to a reactor, opening a hatch to do an internal inspection, etc. With every equipment opening there is a risk and care must be taken to avoid the associated hazards.

There are also unintentional equipment openings possible: leaks, material ruptures by overpressure, opening of safety valves, failing pump seals, etc. These situations cannot be exactly predicted and hence avoiding them may not always be possible altogether, but we can think about the consequences and protect against the hazards.

(Over-)pressure protection is a common theme in process safety; it is one of the main causes for disaster scenario's and may have a number of different causes:

*Vapor generated pressure:* examples are boiling liquids (caused by external heat input such as a fire for example) who create pressure or reactions / decompositions producing vapor components.

*Liquid generated pressure:* in liquid systems an overpressure can be generated by the fact that the density of a liquid is lower with higher temperature; a closed-in liquid that heats up creates very high pressure on the system it is in. Also closing of valves may cause a pressure wave; if the valves closes fast the inertia of the liquid causes it to "crash" against the closed valve which in turn produces a pressure wave running from the valve to the rest of the system. This phenomenon is called liquid or water hammering and is actually very familiar to anyone living in a house with an old water-piping system: if the water tap is closed too fast (a washing machine's automated valve for example) you will hear the "bang!" of the water hammering.

*Equipment generates pressure:* a pump generates a certain pressure which is at its highest when the pump runs against a dead end. This is called dead-heading of a pump and can cause serious consequences if the system cannot handle the maximum pressure of the pump. In case of positive displacement pumps there is actually no maximum pressure point and system cannot be made strong enough; they will always need a form of pressure protection. Backflow from a part of the process under higher pressure may also be a cause. Fluids always flow from high to low pressure and do not stay in one place simply because it is the intent of the design.

Process designers have to protect against all possible forms of overpressure and for this reason many process equipment pieces have safety systems installed on it. This may be control systems that control the process to stay away from an overpressure situation but it may also be a physical device on the equipment which has the advantage that it will also operate when for example the power (to the control system) fails. Actual physical protection against overpressure (or vacuum) may be done using:

*Pressure safety valve:* (usually) a spring operated valve that opens when the process pressure exceeds the set pressure of the valve. It a mechanical device that automatically reliefs overpressure when needed.

*Vacuum relief valve:* more or less the same principle as the pressure safety valve but the pressure gradient is reversed; if the vacuum inside the equipment is too deep the outside pressure will push against the spring and opens up the valve relieving the vacuum.

*Rupture disk:* this is a simple and robust device that actually is exactly what its name says; a disk, a piece of metal, which will rupture at a given – known – pressure. It may be used in both overpressure and vacuum cases.

The above physical protection devices all basically violate rule #1 of process safety: whatever is inside needs to stay inside! But at least they have the advantage that it is known in advance where the material inside the process will come out in case of overpressure. With an equipment rupture or failure it is not known until it happens. The outlet of pressure safety devices can be routed to a safe location such as a flare system, a vent stack, etc.

Other safety equipment commonly used in plants are automated valves (automatically opening or closing in case of emergency and/or in case of loss of power), check valves (backflow protection), control and alarm systems (basic process control systems with warnings and alarms in case of deviating conditions) and safety instrumented systems (instruments that trigger automated responses).

## 5.2 Safer Process Design

So far the discussion has been on how to mitigate risks with process safety equipment or safe guards. But there is also the possibility to design a plant in such way that even the worst case can be handled by the designed equipment. Or to design the plant to minimize the potential hazards or risks.

We call this Inherent Safe Design and this may be defined as follows

> *The essence of inherently safer approach to plant design is the avoidance of hazards rather than their control by added-on protective equipment*

In simple term, described by Trevor Kletz in “plant design for safety – a user friendly approach, 1991”

> *What you don’t have can’t leak”*

There are 5 different approaches to inherent safer design:

1. Minimization or intensification: this approach is aimed at reducing inventories of hazardous materials and energy used in such way that leaks from equipment present a minimal hazard. An example could be to eliminate the storage of liquefied chlorine gas in between the chlorine plant producing it and the ethylene di-chloride plant using it as a raw material.

2. Substitution: the approach is to use alternate materials that are less hazardous or alternate processes that operate in less hazardous conditions. Examples of substitution: Producing halogenated polymers by conducting the polymerization step prior to the halogenation step avoiding the manufacture and handling of hazardous halogenated monomers, or In manufacturing acrylonitrile, using propylene and ammonia as raw materials instead of acetylene and hydrogen cyanide, or Water based paints and adhesives in place of solvent based material, or Aqueous or dry flowable Ag formulations instead of organic solvent formulations, or the use of water or steam as heat transfer medium rather than flammable or combustible oils or the use of Mg(OH)2 slurry for pH control rather than sodium hydroxide.
3. Moderation or attenuation: the approach is to try to operate the process under conditions that are closer to ambient conditions. Examples are the use of catalyst to allow the process to operate at a lower temperature and/or pressure, or the replacement of 36 % hydrochloric acid by 17% hydrochloric acid as feedstock in an aqueous HCl plant thus reducing the partial pressure by over 100 times while only doubling the number of deliveries.
4. Limitation of Effects: in this approach the aim is to limit the impact (consequences) of any material or energy released through plant siting, equipment layout or other engineered systems. Examples are to limit the dikes area for a spill containment of a volatile materials thus reducing the surface area and with that the evaporation rate.
5. Simplification and error tolerance: with this approach the design process is to eliminate unnecessary complexity, reducing the opportunities for error and mis-operation. Examples in this approach are to design equipment to withstand all possible min. and max. pressure of upsets and scenario’s thus eliminating a need for a pressure safety valve or other protective device. Another example is to minimize the use of “leaking” elements such as looking glasses, sample valves, flanges, etc. or to eliminate equipment at all if possible (what isn’t there cannot leak).

## 5.3 Process Risk Assessment

Every plant poses hazards. They are everywhere but they are not always recognized until something happens. As the impact of incidents involving a chemical plant can be quite dramatic it is essential to identify potential hazards and reduce the associated risk well in advance of an accident.

For each process in a chemical plant one has to ask these questions:

- What are the hazards?
- What can go wrong and how?
- What are the consequences?
- What are the chances?

The first two questions represent hazard scenario identification whereas the last two questions represent the risk assessment. It tries to estimate the odds the incident will happen and the consequences if it does. These consequences could include human injury of loss of human life, damage to the environment or loss of production and capital equipment.

The process of assessing the risks associated with the plants process has defined steps as illustrated in Figure 22.

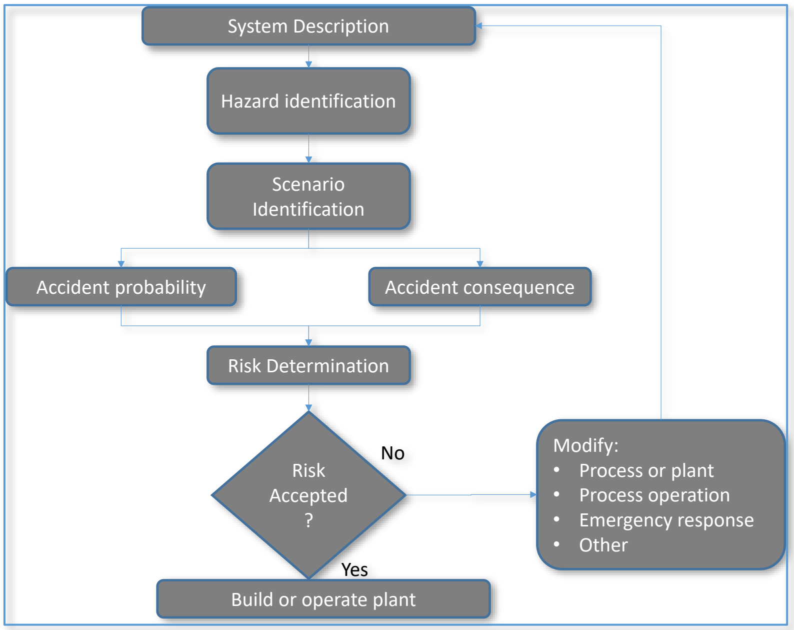


*Figure 22: Steps in a risk assessment procedure*

After a detailed description of the process is made, the hazards are identified. The various scenarios by which an accident can occur are then determined. This is followed by a concurrent study of the consequences of the scenarios and the probability of the accident. With both probability as well as consequence defined, a risk assessment can be done. If the risk is acceptable, then the study is complete and the process is operated. If the risk is unacceptable, modifications need to be made to the system and the new, modified, system undergoes the same procedure again.

An important step in the process of Figure 22 is the decision point: Is the risk acceptable?

Each organization using this procedure needs to have suitable criteria to answer this question which have to be acceptable to the governing authorities as well.

### 5.3.1 Identifying Hazards and Scenarios

For identifying hazards there are a number of structured tools available such as

- Checklist methods,
- Hazard Surveys, for example using tools like the Dow Fire & Explosion Index and Dow chemical Exposure Index,
- Brainstorming methods,
- What if-analysis,
- Hazard and operability (HAZOP) studies, and

- Failure Mode and Effect analysis (FMEA).

The main purpose is to identify potential hazards and scenarios that may lead to an incident. Some of these tools are explained below.

### 5.3.1.1 Checklist method

A process hazard checklist is simply a list of all possible problems and areas that need to be checked. The list serves as a reminder of all the problems that are known. It can be used in the design phase of a project to identify design hazards or it can be used before operating a process. Checklists are widely used in aviation; airline pilots go through checklists before take-off to ensure all system are working properly.

The checklist is only as good as its content; a significant effort should be put into developing the right questions. The design of a checklist depends on its intent; a checklist intended for use during the initial design of the process will be considerably different from a checklist used for a process change.

Checklists should be used only in the preliminary stages of the hazard identification and should not be used as a replacement for a more complex hazard identification procedure.

### 5.3.1.2 Hazard Surveys

Hazard surveys can be a simple as an inventory of hazardous materials in a facility or more complicated using tools such as the Dow Fire & Explosion Index (F&EI) and Dow Chemical Exposure Index (CEI) which are two popular forms of a hazard survey. Both these methods is a calculation of a single index from specified input to rank the hazards of different units and equipment; the higher the calculated index, the bigger the hazard. The F&EI rates the relative hazards related to storage, handling and processing of explosive and flammable materials. The CEI is a method to rank relative acute health hazards.

The Dow F&EI can be used to determine the consequences of an accident, see Figure 23.

| Dow Fire & Explosion index | Degree of Hazard |
|---|---|
| 1 - 60 | Light |
| 61 – 96 | Moderate |
| 97 – 127 | Intermediate |
| 128 – 158 | Heavy |
| 159 and above | Severe |

*Figure 23: Determining the Degree of Hazard from the Dow F&EI*

### 5.3.1.3 Hazard & Operability Study (HAZOP)

The Hazop study is a formal procedure developed to identify hazards in a chemical process facility. The method is effective in identifying hazards and is well accepted in the (chemical-) industry.

The basic idea is to let the mind go free in a controlled manner in order to consider all the possible ways that a process and its operation can go wrong. It is in essence a structured brainstorm and addresses questions like: “what can go wrong? What are the causes? What are the consequences? What measures can be taken to mitigate the risk?”

The method requires a team of people with good knowledge of the design of the plant and the way it is operated. They also have to have an open mind and be able to think outside the box in order to spot things that might go wrong (even though they so far never have gone wrong..). A Hazop study can takes considerable time to complete and follows these steps:

1. Gather detailed process information, chemistry, flowsheets and operational procedures.
2. Pick a flowsheet and break it into a number of “nodes”; a process unit such as a tank, a connecting pipeline system, a reactor, or an operating instruction.
3. Describe the intent of the node including normal process conditions such as temperature / pressure ranges in normal operation, composition of the material, etc.For example: vessel V-1 is designed to store the benzene feedstock and provide it on demand to the reactor.
4. Pick a process parameter: flow, temperature, pressure, concentration, pH, viscosity, state, agitation, volume, reaction, sample, component, etc.
5. Apply a guideword to this parameter. There are a number of different guidewords: No (not, none), More (higher, greater), Less (lower), partial, as well as, part of, reverse, other than, sooner than, later than, where else. For example for parameter flow this yields to: more flow, less flow, no flow, reverse flow, etc. etc. This generates a list of deviations from the original design intent.
6. If the deviation is applicable, determine possible causes and note any protective systems
7. Evaluate the consequences of the deviation (if any)
8. Recommend actions to improve and/or mitigate the hazard.
9. Record all information.

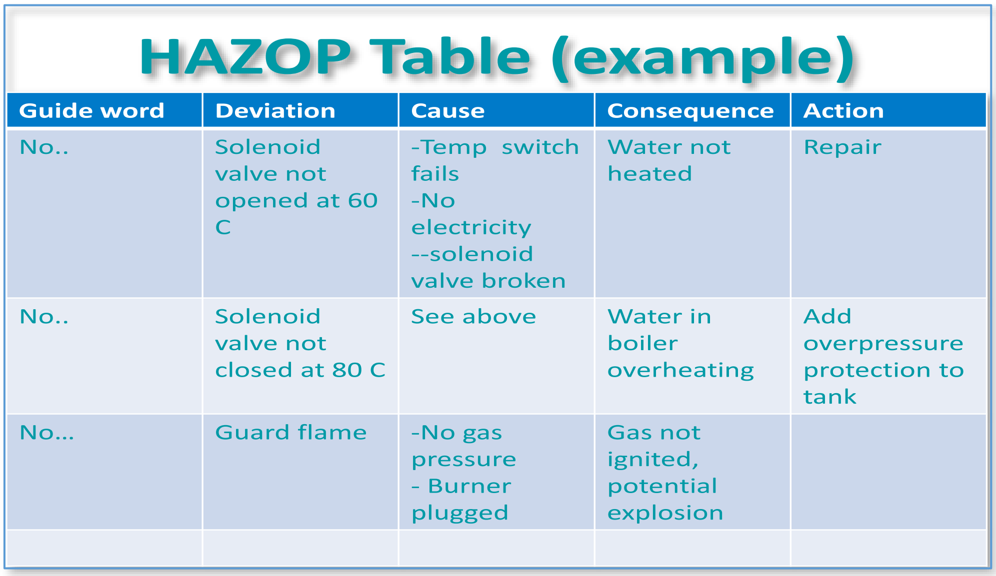
The guidewords are not randomly chosen they originate from a meaning:

- No / not: complete negation of the intention
- More higher / greater: quantitative increase
- Less / lower: quantitative decrease
- As well as : qualitative increase
- part of: qualitative decrease
- Reverse : the logical opposite of
- Other than : complete substitution
- Sooner than: too early or in the wrong order
- Later than: too late or in the wrong order

- Where else: in additional locations

In a Hazop study the team applies all guidewords to all nodes identified and studies the generated deviations. It is likely that there are a number of similar deviations in the total list as nodes are connected. This can make the study a bit boring whilst still consuming a lot of time. At the same time there will be a number of combinations of guidewords and parameters that do not make sense at all. However, the structured approach will ensure that no deviations are overlooked and virtually all possible scenarios can be found. Modern approaches to the Hazop method work out which combinations of guidewords/parameters make most sense for a give node (e.g. for a process vessel or a process pipe) in advance so that scenario lists can be generated using a software approach.

The result of the guideword/parameter combination study is usually recorded in a table. An example is given in Figure 24.



**HAZOP Table (example)**

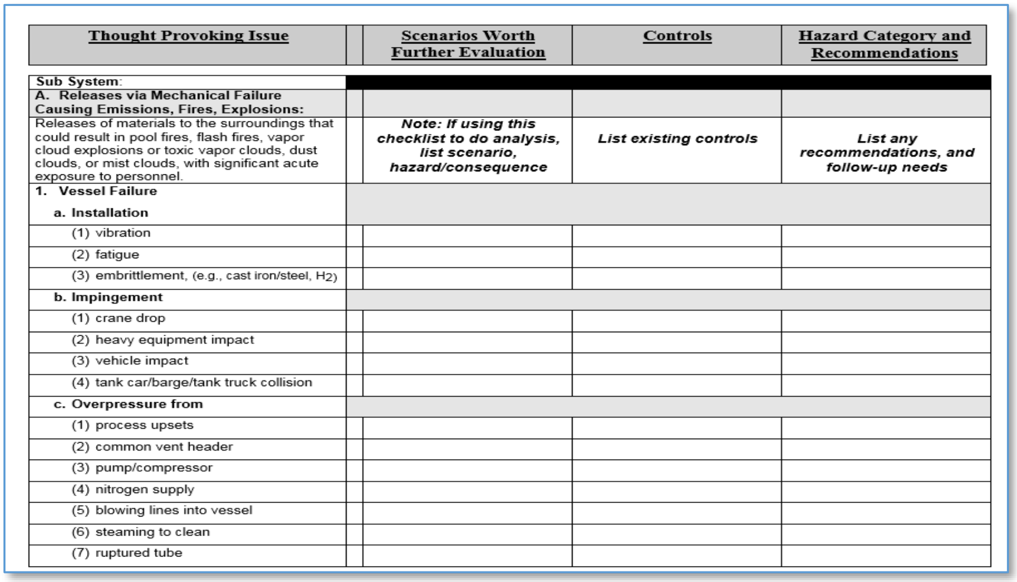
| Guide word | Deviation | Cause | Consequence | Action |
|---|---|---|---|---|
| No.. | Solenoid valve not opened at 60 C | -Temp switch fails<br>-No electricity<br>--solenoid valve broken | Water not heated | Repair |
| No.. | Solenoid valve not closed at 80 C | See above | Water in boiler overheating | Add overpressure protection to tank |
| No... | Guard flame | -No gas pressure<br>- Burner plugged | Gas not ignited, potential explosion | |
| | | | | |

*Figure 24: Example of a Hazop Worksheet*

## 5.3.1.4 What-If analysis

This is a less formal method of identifying hazards and applies the words "What if…" to a number of areas of investigation. For instance, the question might be: What if there is no flow? Or what if the flow stops? The analysis team then decides what potential causes there might be and what the consequences are.

The What-If method can also be used as a sort-of checklist: with a preset list of all types of equipment, instruments, procedures, etc. one can check off if there is a consequence to be found if the relevant piece or unit is missing or malfunctioning; a thought provoking list of potential failure modes that may / may not be applicable. For an example see Figure 25.

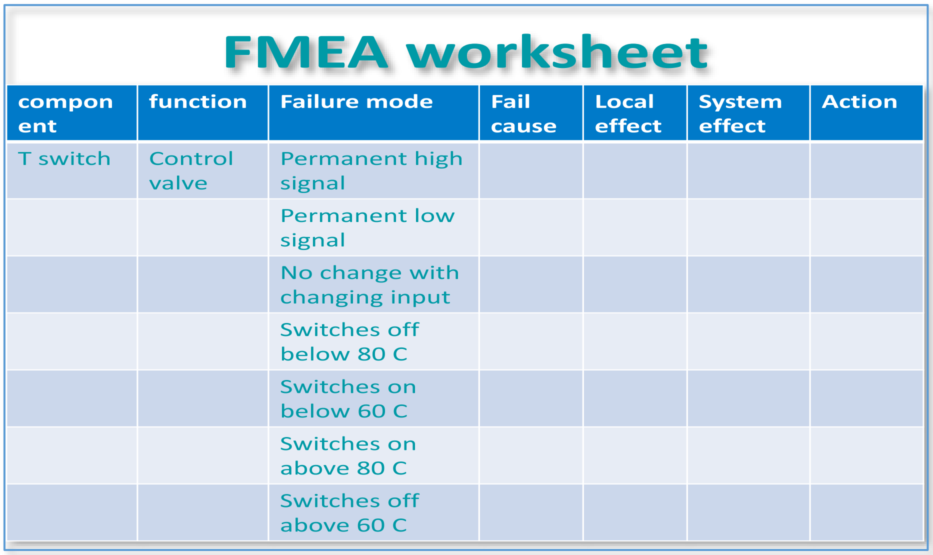


| **Thought Provoking Issue** | **Scenarios Worth Further Evaluation** | **Controls** | **Hazard Category and Recommendations** |
|---|---|---|---|
| **Sub System:** | | | |
| **A. Releases via Mechanical Failure Causing Emissions, Fires, Explosions:** | | | |
| Releases of materials to the surroundings that could result in pool fires, flash fires, vapor cloud explosions or toxic vapor clouds, dust clouds, or mist clouds, with significant acute exposure to personnel. | ***Note: If using this checklist to do analysis, list scenario, hazard/consequence*** | ***List existing controls*** | ***List any recommendations, and follow-up needs*** |
| **1. Vessel Failure**<br>**a. Installation** | | | |
| (1) vibration | | | |
| (2) fatigue | | | |
| (3) embrittlement, (e.g., cast iron/steel, $H_2$) | | | |
| **b. Impingement** | | | |
| (1) crane drop | | | |
| (2) heavy equipment impact | | | |
| (3) vehicle impact | | | |
| (4) tank car/barge/tank truck collision | | | |
| **c. Overpressure from** | | | |
| (1) process upsets | | | |
| (2) common vent header | | | |
| (3) pump/compressor | | | |
| (4) nitrogen supply | | | |
| (5) blowing lines into vessel | | | |
| (6) steaming to clean | | | |
| (7) ruptured tube | | | |

*Figure 25: (part of a) What-If checklist example*

### *5.3.1.5 Failure Mode & Effect Analysis (FMEA)*

A methodology that has been designed for use oriented towards pieces of equipment is the Failure Mode & Effect Analysis or FMEA. This method tabulates a list of equipment in the process along with all the possible failure modes for each item. The effect of the particular failure mode is then considered with respect to the process. See Figure 26 for an example FMEA worksheet.



**FMEA worksheet**

| component | function | Failure mode | Fail cause | Local effect | System effect | Action |
|---|---|---|---|---|---|---|
| T switch | Control valve | Permanent high signal | | | | |
| | | Permanent low signal | | | | |
| | | No change with changing input | | | | |
| | | Switches off below 80 C | | | | |
| | | Switches on below 60 C | | | | |
| | | Switches on above 80 C | | | | |
| | | Switches off above 60 C | | | | |

*Figure 26: Example of Failure Mode & Effect Analysis worksheet*

This method however can also be applied to other processes and operational procedures. In that case the work process of the operational procedure is broken down in steps and for every step the question is asked “what can go wrong?” The consequences of those failure modes is further studied and mitigating actions recommended.

## 5.3.2 Assessing Risk and Consequences

Now that (potential) scenarios and failure modes have been qualitatively identified it is necessary to quantify the risk involved in those scenarios. See also Figure 22 again: after scenario identification comes probability analysis and consequence analysis.

For estimation of the probability we can use tools like the fault- tree analysis and the event tree.

### *5.3.2.1 Fault Tree Analysis (FTA)*

Some scenarios sound far-fetched and strain credibility. However, history has shown us that incredible chains of events can and do happen. Even so, we often find ourselves scratching our heads and asking, “What are the odds of that??” Well, Fault Tree Analysis (FTA) tries to answer that very question.

Fault Tree Analysis is a method for estimating the fault frequency/probability of an undesired state of a system. It was developed in the 1960’s and initially used to assess the risk of placing nuclear weapons on planes. Just think of the risks associated with transporting a nuclear weapon. Not only are there risks at the points of loading and unloading, but the aircraft will surely pass near populated areas. This makes the consequences change during the process. How do you account for that? Well, the answer is FTA.

FTA is a logic model that illustrates combinations of equipment failures and system errors that would cause a specific, defined failure. This is best explained with an example, see also Figure 27.

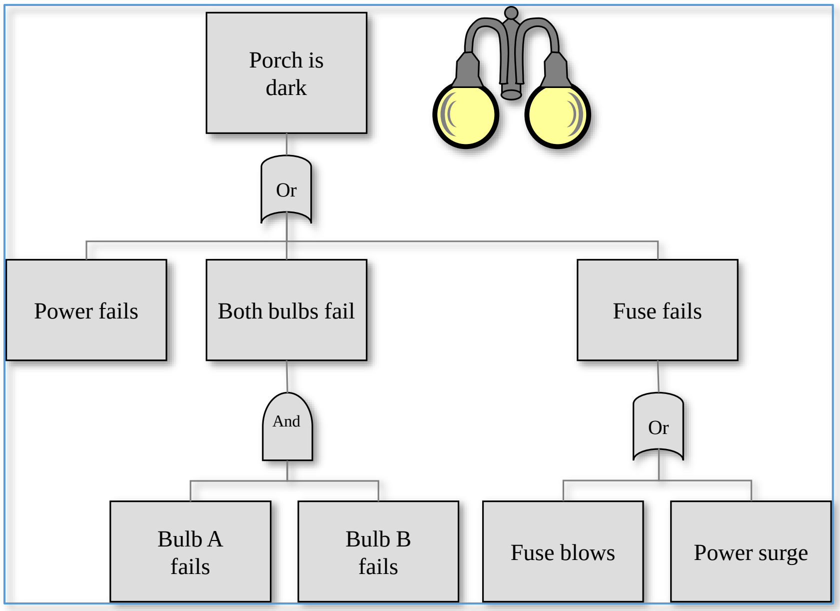


*Figure 27: FTA for a failing porch light*

Consider the situation that a porch has been equipped with a light consisting of two bulbs. However, we find ourselves in the dark on the porch: this is called the top event of the tree and the scenario for which we try to find the answer to the question "what are the odds of that happening?"

First, reasons for this event are established: the fuse might have failed causing loss of power to the bulbs or the power has failed altogether (and all lights are out) or both bulbs have failed. In the scheme they connect to the top event with an OR-gate; one of these failure modes will cause the event above.

The events below the top event are called the intermediate events, if they too can be caused by other events. For example the event that both bulbs fail: it is caused by failure of bulb A AND failure of bulb B. They are connected to the event above using an AND-gate: both events must occur in order to cause the event above.

The power failure, the failure of bulb A, the failure of bulb B, the blowing of the fuse and the power surge are called the basic events.

Fault Tree Analysis is not just another way of drawing a chain of events; it's also a quantitative method to estimate the odds of the top event happening. For this we need to find the failure rates of the basic events, which are often known from literature or experience. For example one could find out how many times there has been a power surge in that particular area and calculate the frequency of that event occurring. Or find data on bulb failure rates from the manufacturer of the bulbs.

With the probability data of the basic events known one can calculate the probability of the top event; half of the needed data to estimate the risk of an event. All we need now is to know the consequences.

### *5.3.2.2 Event Tree Analysis and the Bow-Tie Diagram*

A single event may have several outcomes, depending on all kinds of factors, but can we predict the various types of outcome? This is what an Event Tree Analysis is trying to establish.

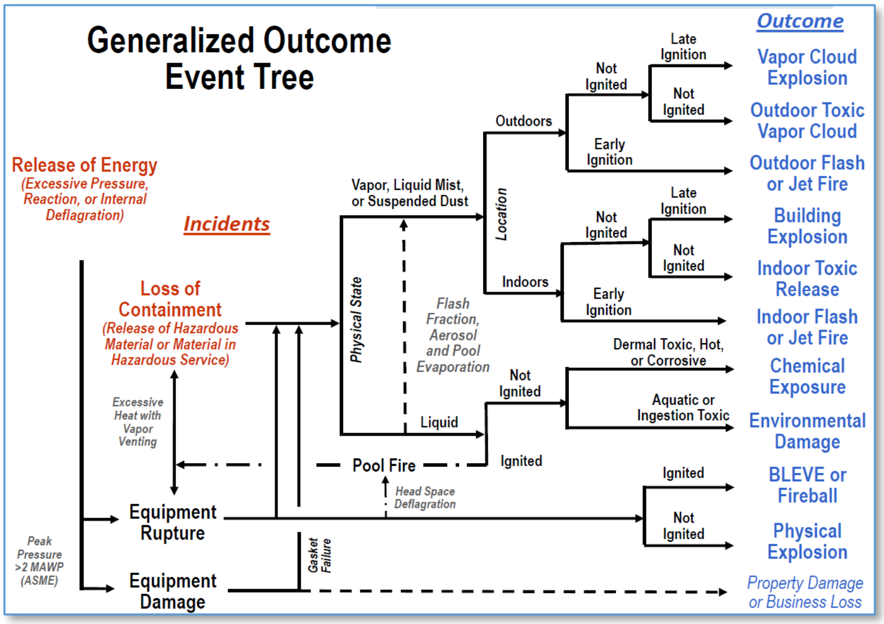


*Figure 28: Example for an Event Tree: a generalized outcome event tree for a release of energy*

To illustrate this, see Figure 28. In this scheme is the generalized event tree given for a Release of Energy in a chemical process, such as a release of excessive pressure, -of a (runaway) reaction or an internal deflagration. The release of the energy may lead to a rupture of the equipment or to some other equipment damage, may be not causing a loss of containment. The materials releases may or may not be ignited leading ultimately to some sort of fire and/or explosion or an exposure to the chemical released.

Even trees and fault trees have some similarities. The Event Tree begins with an initiating event and works his way toward the top event (induction). The Fault Tree begins with the top event and works his way back to the initiating events (deduction). They can be combined as they share the initiating event. Combining them leads to a scheme as given in Figure 29. The combined trees give a complete picture of an incident; from its initiating event all the way to its final outcome. Probabilities and frequencies are attached to these diagrams.

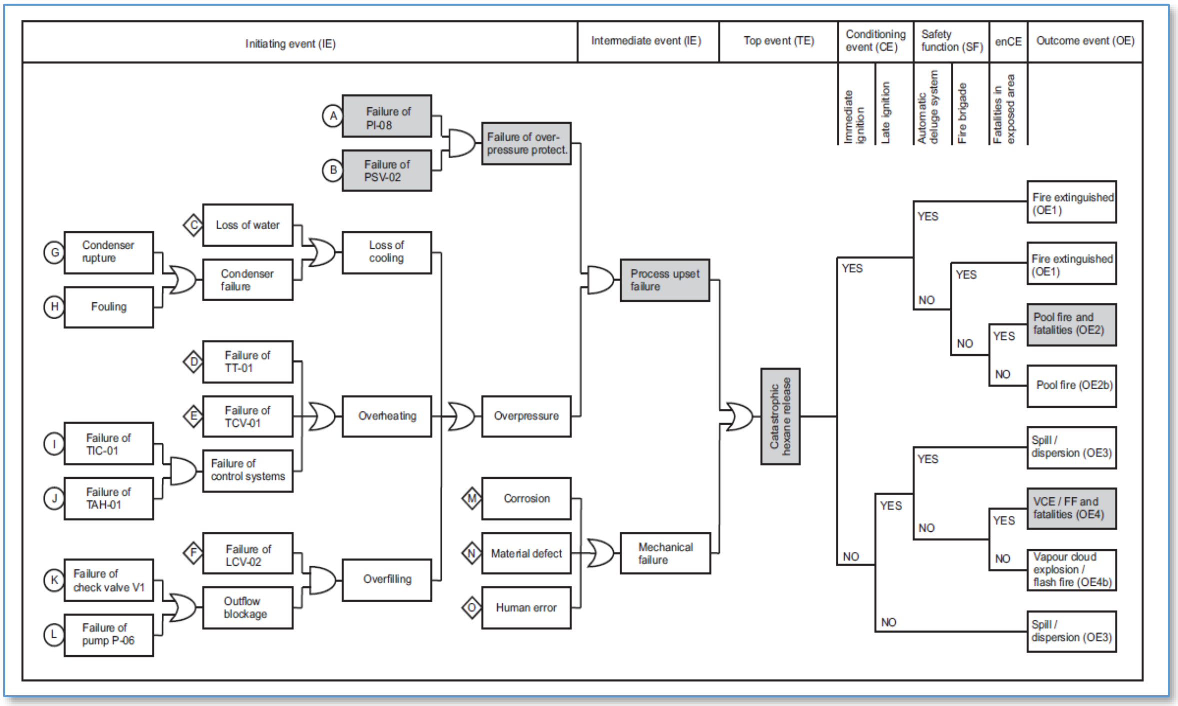


*Figure 29: Combination of a fault tree + even tree for an example scenario*

The scheme of Figure 29 bears big similarities with something called the Bow-Tie diagram, see Figure 30. In this method all events leading to a hazardous scenario are studied as well as all possible outcomes of that scenario and the protective measures or control measures that are in place to prevent a scenario from happening.

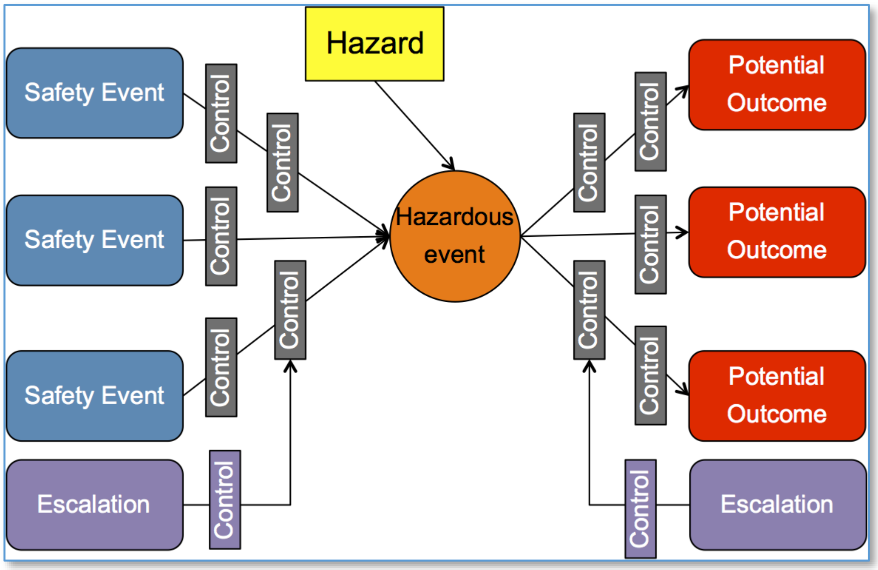


*Figure 30: Generalized Bow-tie diagram*

### 5.3.3 Risk Evaluation and Management

As stated earlier, risk is the product of probability of occurrence of the incident and the consequence of it. When it comes to accepting risk we have the tendency to accept low consequence incidents more often than high severity incidents. This can be shown graphically in Figure 31.

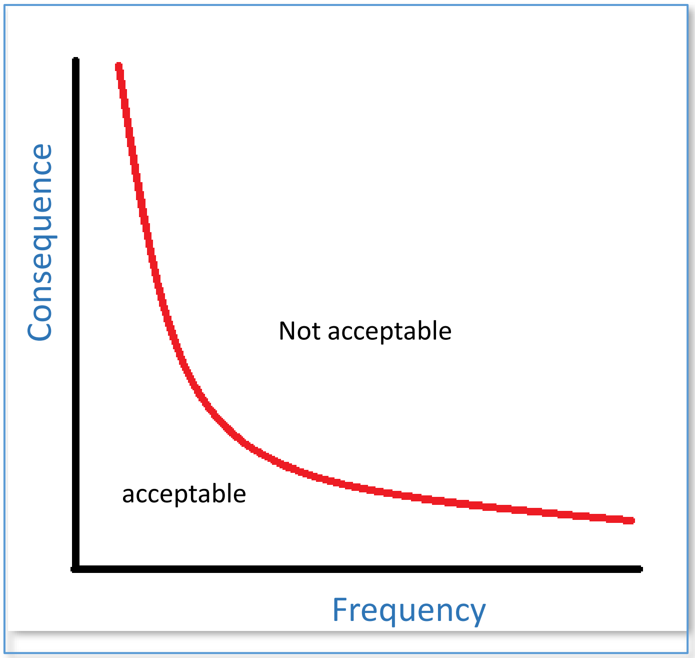


*Figure 31: General Description of risk.*

This curve is a matter of choice; each company will have its own level of acceptable risk. The actual risk is usually determined using a quantitative risk analysis (QRA) and compared against the companies acceptable risk level.

In general, QRA is a relatively complex procedure that requires expertise and substantial commitment of resources and time. In some instances and for more day to day risk analysis questions this complexity may not be warranted; then the application of a Layers of Protection Analysis (LOPA) may be more appropriate.

#### *5.3.3.1 Layers of Protection Analysis*

A Layers of Protection Analysis (LOPA) is a semi-quantitative risk assessment that approximates the risk contributed by an undesired event or scenario (i.e. a story that describes a very particular event sequence resulting in an undesired outcome). LOPA uses order of magnitude estimates for event frequencies, consequence severity and the Probabilities of Failure on Demand (PFD) of Independent Protection Layers (IPLs).

LOPA builds on process hazard analyses such as What-If Analysis and HAZOP studies. It uses information various sources in the determination of whether there are sufficient layers of protection identified to protect against the occurrence of an undesired event. LOPA is most often used to determine whether a given set of IPLs will mitigate a scenario sufficiently to meet the company's risk criteria. Alternately it can be used to estimate the frequency with which an event would occur given the conditions stated including integrity of all Independent Protection Layers credited.

The basic thought of LOPA is that specific layers of protection lower the frequency of a specific accident scenario. It is often graphically shown with the so called LOPA-onion, see Figure 32.

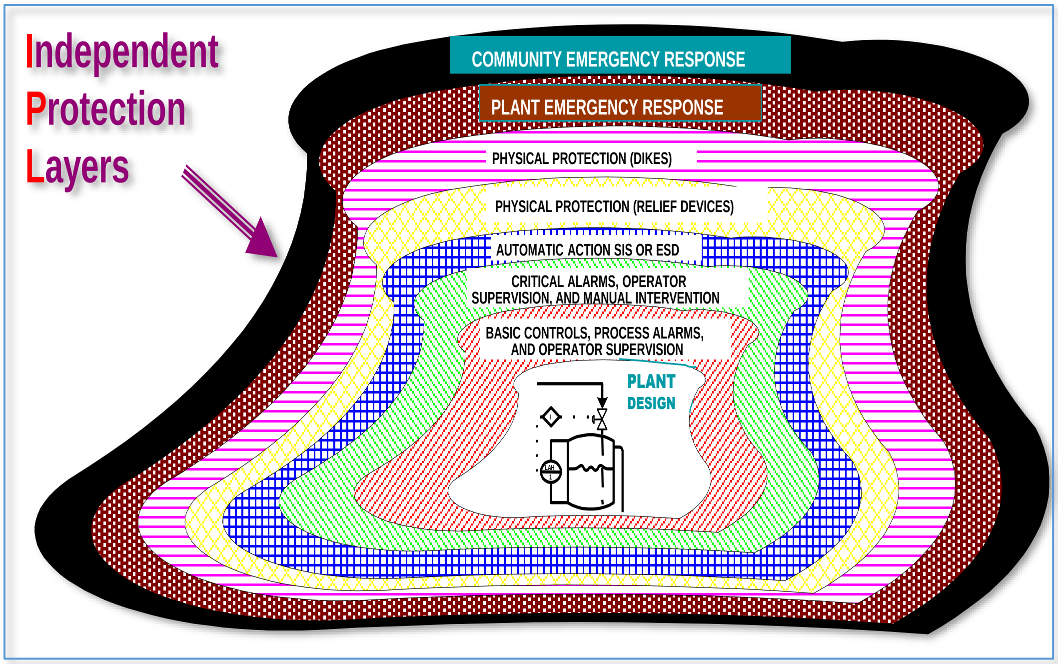


*Figure 32: The LOPA onion: Layers of Protection lower the frequency of a specific accident scenario*

The LOPA method assumes that any layers of protection have a failure chance and an accident might occur if all failures line up exactly right. More commonly this is depicted using the Swiss cheese model, see Figure 33.

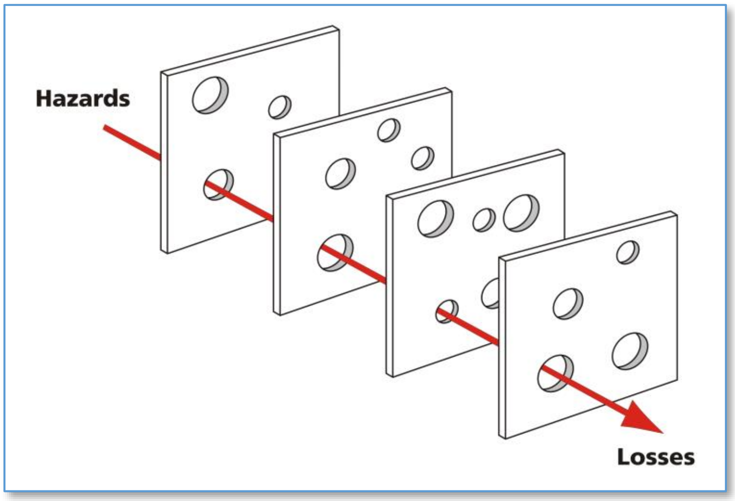


*Figure 33: Generalized Swiss Cheese model.*

In the LOPA method the probability of event occurring as well as probability of protection systems failing is estimated using more generalized failure rates. For example; in a LOPA analysis it is assumed that a normal process control loop (a combination of a measurement, a controller and a control valve) has a failure rate of $10^{-1}$ failures/year or, translated, a failure of 1 every ten years. Part of the LOPA method is to use tables with standard data on failure on demand probabilities. These generalized failure probabilities are normally estimated conservatively.

All the layers of protection can fail and all have a certain probability of failure on demand. Looking at the Swiss cheese layers of Figure 33 one can then estimate the probability of all those holes in the layers lining up exactly right to “let the hazard through”:

The estimate of the probability of the scenario that is studied with LOPA is actually occurring is the product of all failure probabilities of all the protection layers in place:

$P_{scenario} = PFD_1 * PFD_2 * PFD_3 * \ldots$ for all IPL’s.

Instead of using probabilities the LOPA method uses “credits”: a PFD of $10^{-1}$ gives a credit of 1, $10^{-2}$ gives a 2, etc. This way you can simply add the credits to find the probability of the scenario still happening despite all the layers of protection that are in place. See also Figure 34.

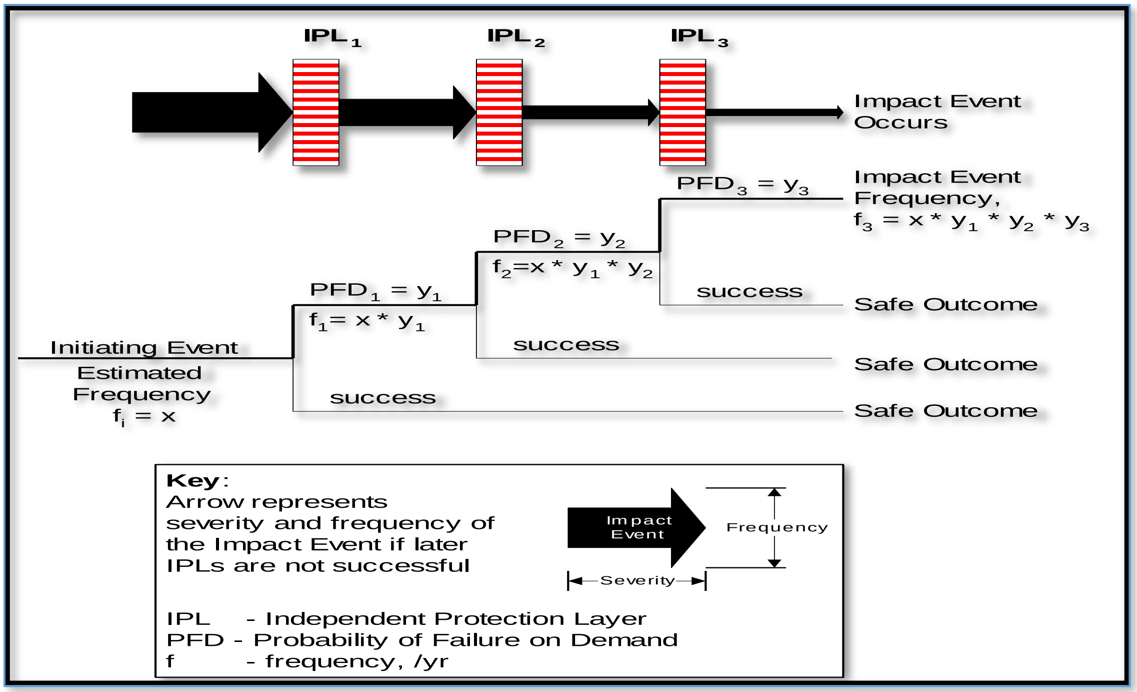


*Figure 34: Protection layer concept in LOPA*

But apart from finding the chance of the scenario happening one also needs a measure for the hazard of the scenario. In LOPA this is done by assigning a LOPA target factor (TF) to the consequence of a scenario.

This target factor can be seen as a translation of the acceptable residual risk of that scenario to a whole number in the same way as the probabilities were translated. In short; a Target factor of 4 indicates that the acceptable residual frequency / probability for that scenario is $10^{-4}$ per year or once every 10.000 years. The target factor is subjective; a company using LOPA will define a list of potential consequences and categorizes them according to severity with a LOPA target factor. This list may differ from company to company.

Comparing the residual risk of the scenario studied with all its protection layers in place to the acceptable risk as defined by severity of the incident will then show whether or not the risk of the scenario is acceptable to the company. In very simple terms:

As long as the LOPA Target Factor is smaller than or equal to the sum of the LOPA credits the probability of the scenario occurring is lower than or equal to the acceptable risk defined. If the sum of the credits is lower than the Target factor then additional (independent) protection layers need to be defined and implemented in order to reduce the risk of that scenario to an acceptable level.

# 6. Safe Handling of chemicals

Chemicals or chemical products can be toxic, flammable, irritating, dangerous for the environment, ozone depleting, etc. etc. and so handling them needs some attention. But the safest way to handle the chemical will depend largely on the actual hazards of it. As seen in section 3. Toxicology, Exposure and chemical risk assessment, there are many ways to be hazardous and on top of that: not all people respond the same way to the hazard. All of that variability would lead to a multitude of ways communicating hazards of chemical to the users of those chemicals and therefore also to a “regulatory mess” if the hazards of controlling risks of chemicals needs to be addressed.

So, in order to have a unified way of addressing the question “When is a chemical or a product considered to be dangerous?” a method has been developed to classify and label chemicals: The Global Harmonized System (GHS) of classification and labeling of chemicals. This system also describes how to communicate hazards of chemicals to its users.

## 6.1 Classification under GHS

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an internationally agreed-upon system, created by the United Nations beginning in 1992 and as of 2015 is not yet fully implemented in all countries. It was designed to replace the various classification and labelling standards used in different countries by using consistent criteria on a global level. It supersedes the relevant system of the European Union, which has implemented the United Nations' GHS into EU law as the CLP Regulation and United States Occupational Safety and Health Administration standards.

The GHS classification system is a complex system with data obtained from tests, literature, and practical experience. The main elements of the hazard classification criteria are:

Physical Hazards: is the chemical explosive, oxidative, flammable, under high pressure, corrosive to metals, self heating, etc.?

Human Health Hazards: is it acutely or chronically toxic, irritating, corrosive, causing mutations or cancer, affecting the hormone system, etc.?

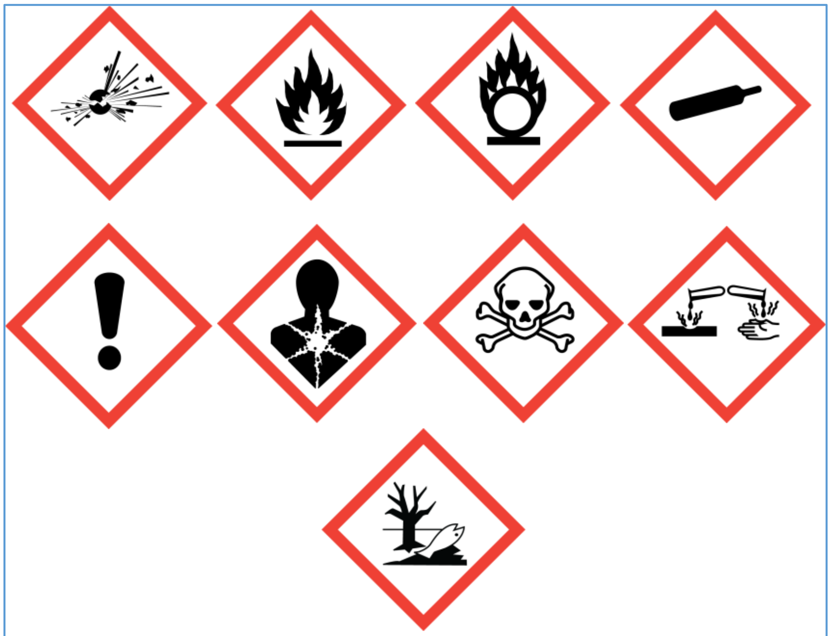
Environmental Hazards: is it acutely toxic to the environment and/or has long lasting effects or destroying the ozone layer?

All three groups of hazards have several types of different hazards defined which have been assigned a standard hazard phrase. A list of these phrases can be found on the UNECE website (http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html) or on Wikipedia (https://en.wikipedia.org/wiki/GHS_hazard_statements). Every hazard type defined in GHS has a standard criterion (with standardized tests) to decide if a chemical is considered to carry that hazard or not.

## 6.2 Labeling and hazard communication under GHS

### 6.2.1. Product Labeling

After classification comes labeling: now that we know what the hazards of the chemical are there must also be a unified way of labeling and communicating these hazards. For this 9 different types of pictograms have been defined, see Figure 35.

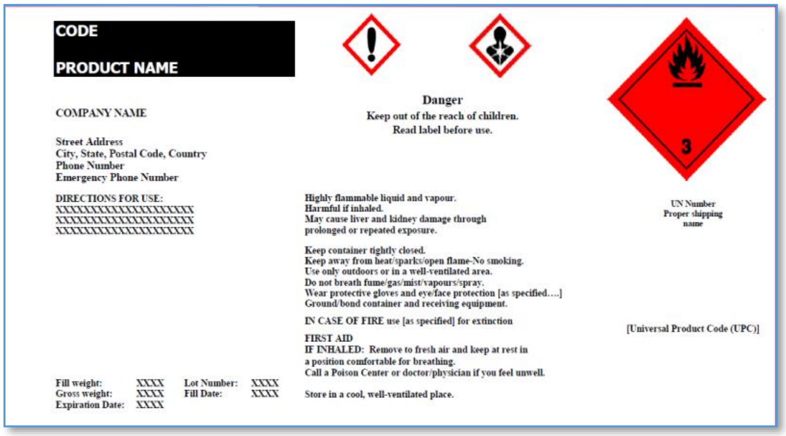


http://www.unece.org/trans/danger/publi/ghs/pictograms.html

*Figure 35: Hazard Pictograms in GHS.*

The top four pictograms are used for physical property hazards, the next four ones are for human health hazards and the bottom one for environmental hazards. These pictograms are used in the same way in every country that has GHS implemented.

Labels on packaged chemicals such as chemicals in drums have been unified too. A typical GHS label is shown in Figure 36.



**CODE**

**PRODUCT NAME**

COMPANY NAME

Street Address
City, State, Postal Code, Country
Phone Number
Emergency Phone Number

DIRECTIONS FOR USE:
XXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXX

Fill weight: XXXX
Gross weight: XXXX
Expiration Date: XXXX
Lot Number: XXXX
Fill Date: XXXX

**Danger**
**Keep out of the reach of children.**
**Read label before use.**

Highly flammable liquid and vapour.
Harmful if inhaled.
May cause liver and kidney damage through
prolonged or repeated exposure.

Keep container tightly closed.
Keep away from heat/sparks/open flame-No smoking.
Use only outdoors or in a well-ventilated area.
Do not breath fume/gas/mist/vapours/spray.
Wear protective gloves and eye/face protection [as specified….]
Ground/bond container and receiving equipment.

IN CASE OF FIRE use [as specified] for extinction

FIRST AID
IF INHALED: Remove to fresh air and keep at rest in
a position comfortable for breathing.
Call a Poison Center or doctor/physician if you feel unwell.

Store in a cool, well-ventilated place.

UN Number
Proper shipping
name

[Universal Product Code (UPC)]

*Figure 36: example of GHS label for a drum containing a chemical*

The label shows the essential information needed such as the details of the company who produced the chemical, the pictograms, the standardized description belonging to the hazard codes – the H-statements, such as "Highly flammable liquid and vapor" in the example of Figure 36 - , the precautionary statements or P-statements – also standardized sentences giving directions on safe handling – and the transport label.

### 6.2.2 Material Safety Datasheet

The GHS regulations also call for the development of a safety document called a Material Safety Datasheet (MSDS) for each chemical that has a hazard classification. The intent of this document is to provide comprehensive information of a substance or mixture for use in the work place. With this document an employer can develop proper worker protection measures specific to his work place and can consider appropriate measures for environmental protection.

An MSDS should be provided for:

- all substances/mixtures meeting GHS harmonized criteria for physical, health and environmental hazards;
- mixtures containing substances meeting criteria for carcinogenicity, toxicity for reproduction or specific target organ toxicity, in concentration exceeding cut-off values;
- other substances/mixtures not meeting the criteria for classification as hazardous but containing hazardous substances in certain concentrations, if required by the competent authority.

But a producer may also develop such a document if the substance/mixture poses some kind of hazards despite not being classified as such.

Every MSDS has the same sections in the same order in the document:

1. Identification: gives identification details such as CAS#, supplier details including emergency contact details and recommended uses or restriction for use.

2. Hazard(s) identification: givens the hazard classification, the GHS labels including precautionary statements and other hazards which do not result in classification.
3. Composition/information on ingredients: all known components that have a hazard classification and that are meeting the minimum concentration threshold for their hazard HAVE to be reported with their chemical identity (CAS#, other identification #), common name and concentration (range). For mixtures the same is true for all hazardous ingredients.
4. First-aid measures: gives information on most important symptoms/effects, both acute and delayed and what special treatment is needed in case of emergency or exposure.
5. Fire-fighting measures: information for firefighters such as suitable extinguishing media, special hazards from fires and protective equipment and precautions for fire fighters,.
6. Accidental release measures: precautionary measures and protective equipment used in accidental releases. Also methods for containment and cleaning of spills are noted.
7. Handling and storage: given conditions for safe storage and handling, including incompatibilities with other materials.
8. Exposure controls/personal protection: gives information of how to control exposure of people to the chemical.
9. Physical and chemical properties: a standard set of properties (that are used in the classification of the product)
10. Stability and reactivity: gives information on reactivity, chemical stability, possible hazardous reactions, conditions that should be avoided, incompatible materials and hazardous decomposition products.
11. Toxicological information: toxicological information on the product and on all mentioned components of section 3 (if applicable)
12. Ecological information: eco-toxicological information, persistence in the environment, bio accumulating potential and/or bio-degradation, etc.
13. Disposal considerations: how to properly dispose of the substance/mixture
14. Transport information: gives transport classification, UN number, transport hazard class, packing group (if applicable), etc.
15. Regulatory information: applicable regulations and regulatory info.
16. Other information.

## 6.3. Transport Safety

Safety considerations in the transportation of chemicals is as important as safety in producing chemicals. For example; an accident involving a tank truck with a flammable liquid will likely result in a big fire or even an explosion with the potential to kill people that are in the immediate area. Another example is an accident with an oil tanker at sea; apart from the flammability risks there is a big risk of endangering the environment as has been proven with several incidents involving oil tankers that polluted large areas of shore with all its wild life.

This is why transportation of dangerous chemicals, in the transport world known as dangerous goods, is heavily regulated. There are different regulations for different types of transport of dangerous goods:

- ADR : road transport,
- RID : rail transport,
- AND : transport in bulk in inland waterways,
- IMDG & IBC codes: bulk sea transport
- ICAO TI: air transport.

The United Nations tries to coordinate and harmonize these regulations.

### 6.3.1 Road Transport

In Road transport classification a chemical is classified as dangerous goods if it meets certain criteria which are not necessarily the same criteria as used in product classification under GHS. The ADR regulation knows 9, numbered, danger classes:

1. Explosive substances
2. Gases
3. Flammable liquids
4. Flammable solids
5. Oxidizing substances
6. Toxic and contagious substances
7. Radioactive substances
8. Corrosive substances
9. Other dangers

These danger classes are communicated on truck carrying chemicals using a Kemler code, see Figure 37. The label actually has 2 numbers: the top number is the Kemler code and the bottom number is the UN number.

*Figure 37: example of truck marking with Kemmler and UN code*

The Kemler code is a number that will tell what kind of hazard the chemical in the truck poses. It works like this:

If the chemical is, for example, most predominantly a flammable liquid then it has hazard class 3 and the number will start with a 3. If that is all the hazard that the chemical carries then the number is completed with a 0 showing 30: flammable liquid. In other words: the second number is giving the next, not main but still important, hazard. A zero would in this case mean that there is no other danger to be considered. However, if the chemical is actually not “just” flammable but very flammable (remember that there are criteria defined on when it is one of these) then the 3 is doubled to show it is very flammable (or very toxic in case of 66, etc.).

Kemler codes are always 2 or 3 numbers long so 3 different hazards can be shown or 2 if one of them is more extreme. Example: a Kemler code of 336 will indicate a “very flammable poisonous liquid” and 663 is a “very poisonous liquid, flammable”. On Wikipedia there is an overview of all Kemler codes:

http://nl.wikipedia.org/wiki/Gevaarsidentificatienummer

The bottom number in Figure 37 is called the UN number. This number has been assigned by the UN and will give insight on the identity of the substance / chemical. A UN number of 1695 for example is choloracetone, stabilized. A list of UN numbers is also on Wikipedia:

http://en.wikipedia.org/wiki/List_of_UN_Numbers

Apart from the Kemler code / UN number sign a truck also carries the labels on the outside so it is clear what is inside the truck and what the dangers are, see Figure 38.

ADR pictograms [ edit ]

ADR pictograms for chemical hazards are based on GHS Transport pictograms and Non-GHS transport pictograms

*Figure 38: ADR pictograms*

For an example on how the labels are used on a bulk tank truck see the picture in Figure 39.

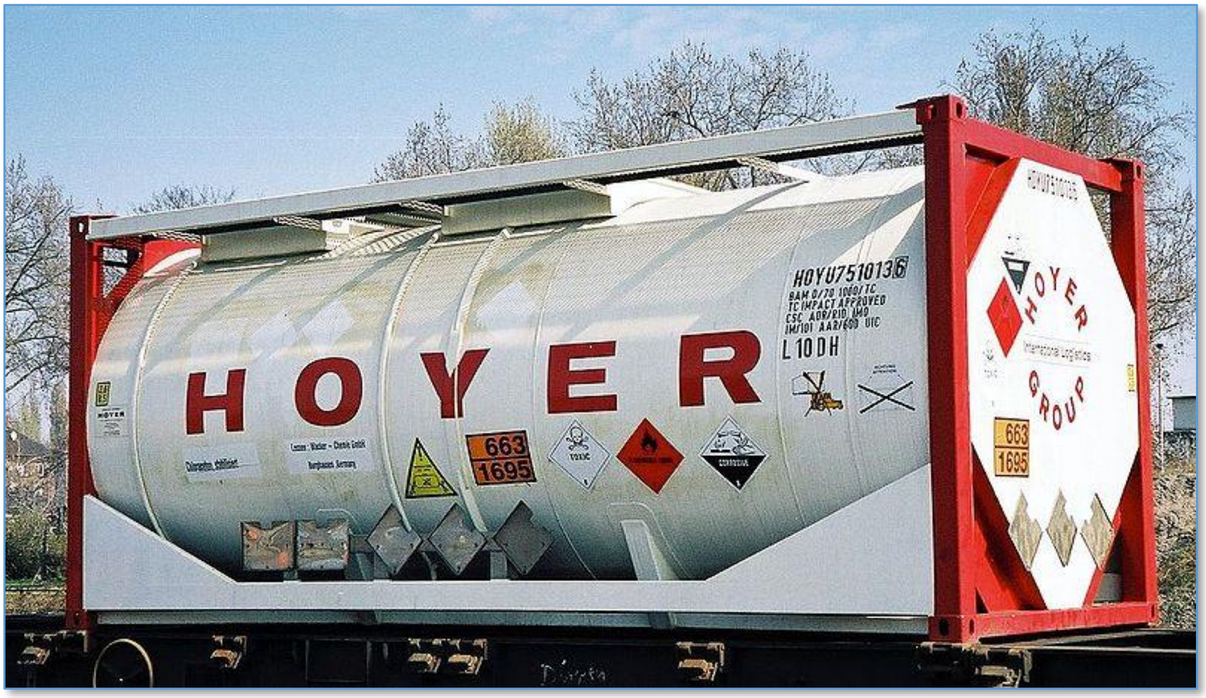


*Figure 39: example picture of a bulk chemical container for road transport*

### 6.3.2. Transport over water

Bulk transport of chemicals over sea is regulated by the IMDG Code: International Maritime Dangerous Goods code. It is developed and maintained by IMO – the International Maritime Organization – which is the United Nations specialized agency with responsibility for the safety and security of shipping and the prevention of marine pollution by ships (see also [www.imo.org](http://www.imo.org) ).

The IMDG code essentially uses the same way of hazard classification as ADR in 9 hazards classes numbered 1-9. However, the labels used are a little different, see Figure 40.

*Figure 40: IMDG labels*

### 6.3.3. Transport through the air

Transport of dangerous goods through the air is highly regulated and often forbidden. The Governing body is IATA – International Air Transport Association (see http://www.iata.org/publications/dgr/pages/index.aspx ). Like with road and water transport the dangerous goods classification knows 9 hazard classes:

- Class 1: Explosives
- Class 2: Gases
- Class 3: Flammable Liquids
- Class 4: Flammable Solids
- Class 5: Oxidizing Substances
- Class 6: Toxic and Infectious Substances
- Class 7: Radioactive Material
- Class 8: Corrosives
- Class 9: Miscellaneous Dangerous Goods

The labeling used in air transport is again similar to the other modes of transport but not identical, see Figure 41.

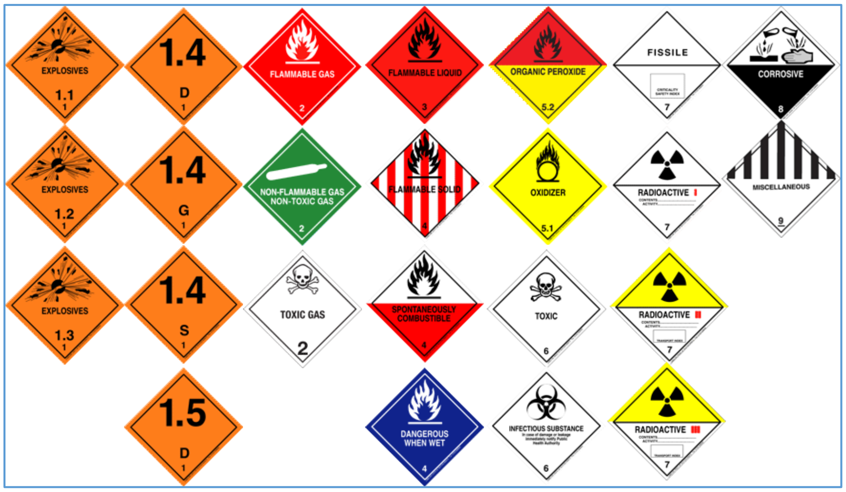


*Figure 41: Transport labels by IATA*

## 6.4 Storage Tank Labeling

When chemicals are stored it is very often in liquid form in a storage tank. When something happens or a fire breaks out at the tank it is important to understand the hazards of the chemical in the tank without having to read all of the information in an MSDS. The national Fire Protection Agency (NFPA) in the US has developed a simple and effective system of labeling that can be used on storage tanks (and other process equipment).

The principle of the labeling is simple; in cases of a fire it is important to know if a chemical is a) fire hazard, or b) an acute health hazard or c) unstable and/or reactive and if there are any other special hazards to consider. All of these hazard groups have a clear marking on the tank with a number ranging from 0 (not hazardous) to 4 (very hazardous). An example of an NFPA tank label is given in Figure 42.

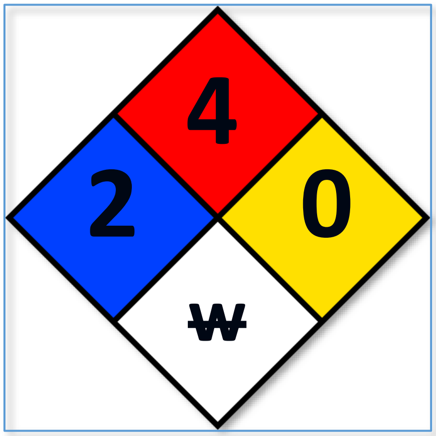


*Figure 42: Example of NFPA tank Label*

The advantage of such a label is clear: it can be read from great distances and immediately gives information on the potential hazards in case of an emergency with the tank (a fire for example).

### 6.4.1. Fire Hazard (red)

The main criterion for assigning a 0 – 4 for the fire hazard (red square) is the flashpoint:

4 – Class 1A: flashpoint less than or equal to 73 F

3 – Class 1B/1C: flashpoint less than or equal to 100 F

2 – Class 2/3A: flashpoint less than or equal to 200 F

1 – Class 3B: flashpoint bigger than 200 F

0 – will not burn.

### 6.4.2. Health Hazard (blue)

For the rating of the health hazard the main criteria are acute health effects of the chemical. The rating criteria has been split for three groups: 1) gases, liquids and vapors, 2) dusts & mists and 3) materials (solids) and for all groups criteria have been set for the various ratings:

| NFPA rating | gases, liquids and vapors | dusts and mists | Materials | | |
|---|---|---|---|---|---|
| | value in ppm | value in mg/l | dermal exposure (mg/kg) | oral exposure (mg/kg) | other effects to skin, eyes, respiratory tract |
| 4 | <= 1000 | <= 0.5 | <= 40 | <= 5 | |
| 3 | <= 3000 | <= 2 | <= 200 | <= 50 | corrosive |
| 2 | <= 5000 | <= 10 | <= 1000 | <= 500 | irritating |
| 1 | <= 10000 | <= 200 | <= 2000 | <= 2000 | mildly irritating |
| 0 | > 10000 | > 200 | > 2000 | > 2000 | nonirritating |

### 6.4.3. Instability Hazard (yellow)

The instability of a chemical in the NFPA rating is a combination of explosiveness and reactivity (with water). The water reactivity originates from the fire-fighting: water is very often used to extinguish a fire and when the chemical reacts violently with it this is important to know (obviously)

The rating goes as follows:

4 – May detonate; unstable at normal temperature and pressure

3 – Shock and heat may detonate; requires initiation source for detonation. Sensitive to thermal and mechanical shock. Reacts explosively with water without heat or confinement.

2 - Violent chemical change; reacts violently with water or forms potentially explosive mixtures with water. Undergoes violent chemical change at elevated temperature and pressure.

1 – Unstable if heated; reacts vigorously with water. Changes or decomposes on exposure to light, air or moisture. Unstable at elevated temperature and pressure.

0 - Stable; stable under fire conditions. Does not react with water.

More information, also about the special hazards that are put into the white part of the diamond can be found on wikipedia: https://en.wikipedia.org/wiki/NFPA_704

## 7. Incident Analysis

Incidents happen. Things that we did not expect occurred and caused an incident with bigger or smaller effect. While all kinds of methods can be applied to find potential incidents before they happen nature can sometimes surprise us with something no one thought about. Next to preventive actions for incidents it is therefore also important to investigate incidents that have happened. So that lessons can be learned and repeat incidents are avoided. This is why incident investigations are done.

Most accidents are investigated in an attempt to find the so called root cause of the problem, but what is a root cause?

The definition of a root cause is: the fundamental underlying reason for a problem. It will cause the problem to happen repeatedly and is not a symptom. When it is removed the problem is fixed permanently. Finally this all needs to be proven with data.

Root cause investigations are done to identify the right thing to solve in case of a problem. This will enable preventing that the same incident will happen again in the future…. Provided we learned from it. A good root cause investigation is not about finding the guilty or the scapegoat and is not a, so called, band-aid solution; it eliminates the true cause of the problem.

To do a good root cause analysis these steps need to be taken:

1. Identify and define the problem; it is important to understand the true problem of an incident in order to work on the right solution. This is easier said than done actually; what is actually the problem may sometimes be overshadowed by some of the side-effects of it.
2. Identify all possible causes of the problem; this requires creativity and use of different methods to establish what could have caused this problem to occur.
3. Determine the probable Root Cause(s); with good judgement and use of knowledgeable people in the field some causes are more likely to have cause the problem than others; these are worth further investigating.
4. Collect and Analyze Data; it is no good having only probable causes and then starting to eliminate them. They have to be proven with data.
5. Confirm the Root Cause; in this step the data gathered or new data is used to prove the direct relationship between cause and consequence … or in this case: problem. Only with proof one can conclude that a cause is indeed a root cause and eliminating it will solve the problem permanently.

As illustration here is an example: a slipping incident: an employee of company A slipped on something in the plant and broke his wrist in the fall.

First some background on the situation: Company A is a company with a very aggressive approach towards safety: Zero Tolerance, Zero Incidents is their motto. The upper management is very clear about their expectations: plant managers are fully accountable and are expected to ensure it will never happen again. The responsible plant manager's safety record is set to zero only 2 days from having a 1 year incident free record. The plant manager sets out to investigate the problem…..

The Plant Manager walked into the plant and found oil on the floor. He called the Foreman over and told him to have maintenance clean up the oil. The next day while the Plant Manager was in the same area of the plant he found oil on the floor again and he subsequently raked the Foreman over the coals for not following his directions from the day before. His parting words were to either get the oil cleaned up or he'd find someone that would! Zero Tolerance, Zero Incidents!!!

Now ask yourself: will this incident never happen again? Was the root cause found and addressed?

Usually there are some causes that will contribute to the outcome or magnitude of the problem but do not eliminate it if they are taken away. These are called contributing causes and are important to know but will NOT solve the problem if they are eliminated; solutions that take away these contributing causes are therefore at best a band-aid solution to the problem.

Causes that have their origin in human behavior and/or in people performance are notoriously hard to find. After all, who wants to admit that they have messed up or did something foolish or even "forbidden"? However, if one assumes that professional people do not break rules on purpose without a reason and actually try to contribute to the success of the company/operation/activity then there is no doubt that it is even more important to understand why people did what they did to find the true underlying reason for their behavior.  Situations like terrorism set aside one can therefore conclude that people involved in an incident should never be blamed or made a scapegoat but a culture of openness should be strived for.

## 7.1 Investigation Tools

In order to find causes there are several different tools available but no one tool will fit all cases. It will depend on the situation what is the best tool. To name a few:

- Brainstorming: having a group of knowledgeable people brainstorm about potential causes
- Cause& Effect diagram or Fishbone diagram (or Ishikawa diagram)
- 5-whys or why-why analysis
- Relations diagram
- ABC and/or BOC analysis (see chapter 1).

### 7.1.1. Fishbone diagram.

A Cause & Effect Diagram, also known as a Fishbone diagram or an Ishikawa diagram, is a tool that is used to chart causes that might lead to a problem. The method has been developed by Kaoru Ishikawa and was originally intended to improve production processes and quality problems.

The method is a strong visualization of the relation between problem and factors that might influence that. An example is given in Figure 43.

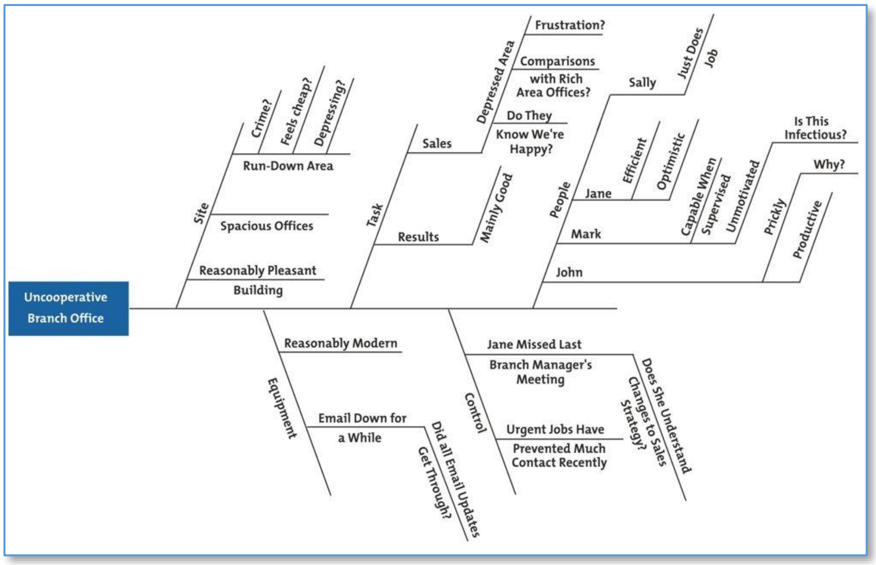


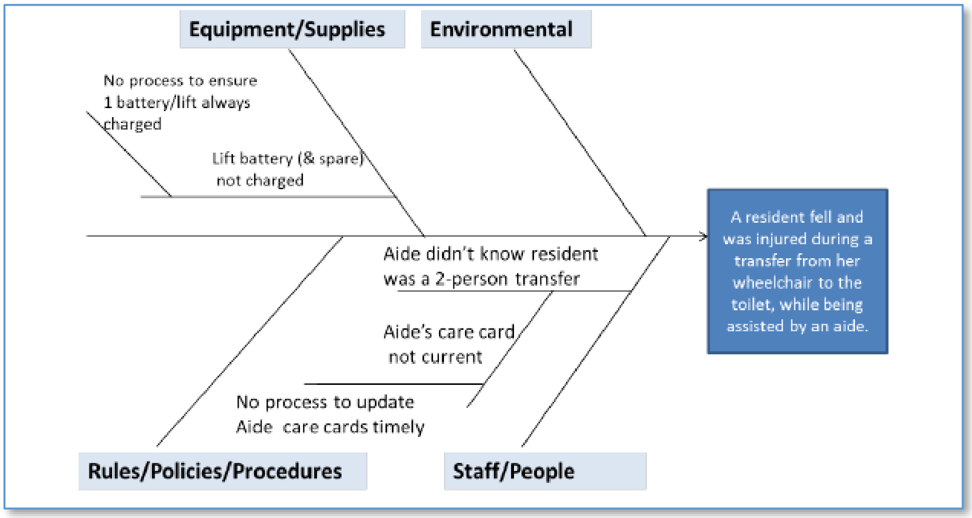
*Figure 43: Example of a Fishbone diagram*

In a way it is organizing a brainstorm approach to finding probable causes of the problem. To use it a team of people need to work together to create potential causes and organize them in groups of similarity. Some causes are underlying other observed apparent causes. Trying to organize the data in a fishbone diagram will show these relationships. For example:

Facts gathered during preliminary investigation:

- Time of fall: change of shift from days to evenings
- Location of fall: resident’s bathroom
- Witnesses: resident and aide
- Background: the plan of care stipulated that the resident was to be transferred with two staff members, or with one staff member using a sit-to-stand lift. Information from interviews: the resident was anxious and needing to use the bathroom urgently. The aide was helping the resident transfer from her wheelchair to the toilet, without using a lift, and the resident fell, sustaining an injury. The aide stated she did not use the lift because the battery was being recharged, and there was no extra battery available. The aide stated she understood that the resident could be transferred with assist of one.

With this information, the team proceeded to use the fishbone diagram to better understand the causes of the event:



The value of using the fishbone diagram is to dig deeper, to go beyond the initial incident report, to better understand what in the organization's systems and processes are causing the problem, so they can be addressed.
In this example, the root causes of the fall are:

- There is no process in place to ensure that every lift in the building always has a working battery. (One battery for the lift on this unit is no longer working, and the other battery was being recharged.)
- There is no process in place to ensure timely communication of new care information to the aides. (New transfer information had not yet been conveyed to the aide. The aide's "care card" still indicated transfer with assist of one for this resident.)

The root causes of the event are the underlying process and system problems that allowed the contributing factors to culminate in a harmful event. As this example illustrates, there can be more than one root cause. Once you have identified probable root causes and contributing factors, you will then need to first prove with data their contribution to the problem and then address each root cause and contributing factor as appropriate.

### 7.1.2. Why-Why Analysis

The why-why analysis is also known as the 5-whys analysis and is based on a very simple principle, often instinctively used by children, method: ask the question "Why?" 5 times for every answer and start with the problem. By the time you get to the fifth level you are getting into the structural issues causing the problem.

An example of a why-why-diagram for trying to identify root causes to a problem is given in Figure 44. The diagram tries to answer a manager asking himself: "Why is making travel arrangements such a time consuming hassle?"

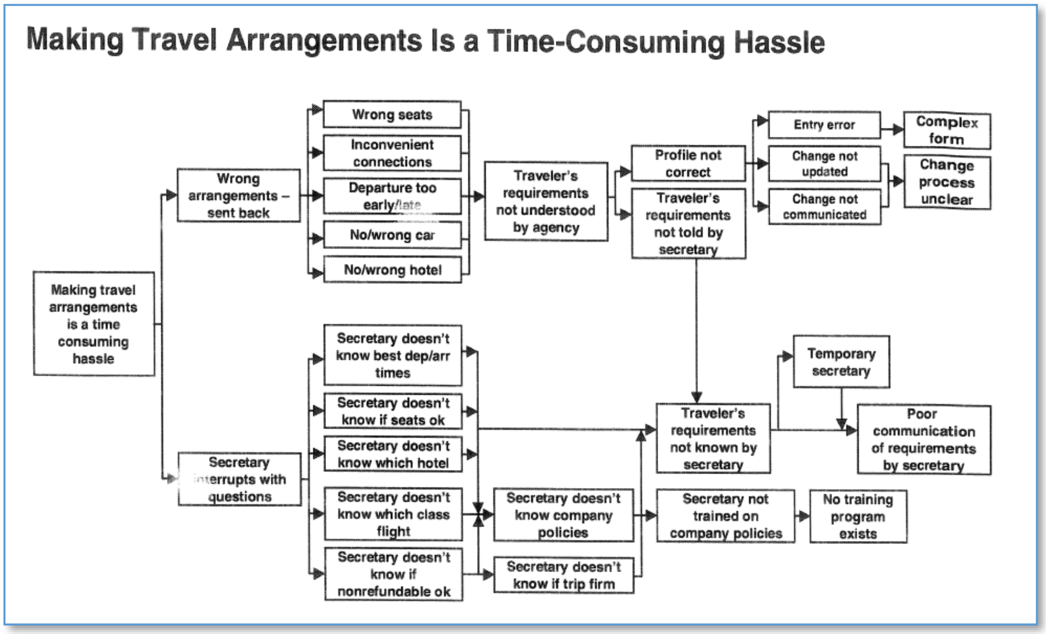


*Figure 44: Example of a Why-Why Diagram.*

The diagram starts left with the problem statement and with every step to the right the question "Why is that?" has been asked and answers were formulated to that question.

To illustrate further let's use why-why to analyze the slipping incident from the introduction to this chapter: a person slipped over something in a plant and broke his wrist.

The plant manager finds oil on the floor and asks the Foreman: **Why** is there oil on the floor ? The foreman answers: there is a leaking gasket.

The plant manager asks: **Why** is the gasket leaking? Is it old? The foreman: no, not old but new. And 4 others gaskets also leak by the way.

The plant manager goes to investigate with maintenance and asks the maintenance leader: **Why** are new gaskets leaking? Is it a bad batch? The maintenance leader doesn't know but advises to ask purchasing about these gaskets. So the plant manager does…. And finds out that actually there have been a lot of issues with this supplier.

The plant manager asks again: **Why** …are we using this supplier if we have so many problems with them?

Purchasing tells him that they were the lowest bidder and so they got the order: Finance VP's orders! So the plant manager goes on to find answers from the Finance VP: **Why** did he order to only accept the lowest bidder?

The answer made the plant manager realize that in fact his own policy is at the root of the problem: the VP answered: "Because you indicated that we had to be as cost conscious as possible... and purchasing from the lowest bidder saves us lots of money."

As demonstrated the why-why technique can be effective in identifying root causes. Sometimes, asking why again does not give a good answer anymore because no one knows… In that case it is necessary to investigate further with other means to find probable causes behind the observed effects.

There is also a downside to endlessly asking why?why?why? Experience has shown that people tend to become impatient after the third why-level but the method is not effective in finding the real causes if it is not driven down at least 5 levels. This is where proper facilitating of the effort is needed to ensure a good outcome.

## 8. Summary

Safety is the practical certainty that no harm will be done. But achieving that is no easy task when dealing with all ins and outs of producing chemicals in a chemical plant. On top of that ther is a subjective choice of what is actually an acceptable risk.

The ideal world would look something like this:

The design of the plant is inherently safe, meaning that it is built to withstand all potential dangerous scenarios.

All possible scenarios that may cause harm are known, their risk understood and controlled.

The normal and abnormal operation of the plant is thoroughly reviewed and evaluated and will stay within preset acceptable limits. The people working in the plant always do “the right thing”.

The maintenance of the plant is done in a way that ensures mechanical integrity in all foreseeable situations.

The effects of the chemicals on the human body and the environment is fully understood and exposure to the chemicals is perfectly controlled or even totally eliminated.

The products of the plant do not need transportation or are transported in such a way that nothing will go wrong.

The practice of today is still far from this ideal which is why incidents happen and tools like Root Cause investigations are needed to learn from them and to prevent them in the future.

Achieving safety in the chemical industry is a continuous effort and will need to be a top priority:

**SAFETY FIRST!**