**Subselection**

**Question:** How should a storage tank with a solution of ammonium nitrate (90%) in water be calculated in the subselection?

**Answer:**
1. Calculate the amount of toxic substances formed at the Adiabatic Steady State Temperature during 10 minutes.
2. Determine the selection number using the amount of toxic substances formed and the limit value of nitrogen dioxide. The factors to be used are $O_1 = 0.1$ (storage), $O_2 = 1$ en $O_3 = 10$ (gas phase).
3. Include the storage tank if the selection number is larger than 0.5 times the maximum selection number.
4. Do not exclude other installations based on the selection number of the storage tank.

**Status:** Concept

**Consideration:** Ammonium nitrate is an oxidising substance. Ammonium nitrate may be important in a risk analysis due to its explosive properties and the release of toxic gases if heated.

An aqueous solution of ammonium nitrate with a concentration of ammonium nitrate more than 90% by mass is a listed substance in BRZO99.

Ammonium nitrate is considered as an explosive substance in the document “Beleidsregels arbeidsomstandighedewetgeving”. Two different types of ammonium nitrate are distinguished, namely ammonium nitrate having a purity larger than 90% and with a content of flammable material less than 0.2% and ammonium nitrate with a content of flammable material more than 0.2%.

Ammonium nitrate is not classified as a toxic substance. However, decomposition of ammonium nitrate results in the emission of toxic gases, especially NO$_x$.

An aqueous solution of ammonium nitrate (90%) is not explosive at ‘normal’ storage conditions, but may release toxic gases if heated. Therefore, an approach would be:

- calculate the amount of toxic substances formed at the Adiabatic Steady State Temperature (ASST) during 10 minutes. ASST is the temperature where the exothermic and endothermic decomposition and dissociation reactions are in equilibrium; for pure ammonium nitrate ASST is close to 290 °C.
- determine the selection number using the amount of toxic substances formed and the limit value of nitrogen dioxide. The factors to be used are $O_1 = 0.1$ (storage), $O_2 = 1$ en $O_3 = 10$ (gas phase).
The method proposed here is not tested in practice and care has to be taken to exclude installations using this procedure. It is therefore suggested that:

If the solution of ammonium nitrate in water has the highest selection number at a location, the solution should be included in the QRA. The selection of other installations should be based on the next highest selection number.

If the solution of ammonium nitrate in water has a selection number larger than 0.5 times the maximum selection number, the solution should be included in the QRA.

If the solution of ammonium nitrate in water has a selection number less than 0.5 times the maximum selection number, in principle the solution does not need to be included in the QRA.

Furthermore, it should be noted that following the Toulouse accident special attention has to be paid to the explosive properties of ammonium nitrate.

**Loss of Containment events**

**Question:** An establishment is situated within the risk contour of an airport. Is this incorporated in the standard failure frequencies?

**Answer:** No, standard failure frequencies are without external impact. If the location specific risk of an aeroplane crash is larger than 10% of the standard catastrophic failure frequency of a tank, the location-specific risk is added to the standard catastrophic failure frequency. The frequency is evenly divided in an instantaneous release and a continuous release of the inventory in 10 minutes.

Example 1: A pressurised tank is situated near an airport between the location-specific risk contours of $1 \times 10^{-7}$ per year and $1 \times 10^{-8}$ per year. In this case, the location specific risk of an aeroplane crash is less than $0.1 \times$ the standard failure frequency of the tank ($1 \times 10^{-6}$ per year), and is therefore not considered.

Example 2: A pressurised tank is situated near an airport at the location-specific risk contour of $1 \times 10^{-6}$ per year. In this case, the location-specific risk of an aeroplane crash is more than $0.1 \times$ the standard failure frequency of the vessel, and the failure frequency of the tank is now $2 \times 10^{-6}$ per year (standard failure frequency $1 \times 10^{-6}$ per year + failure frequency due to external impact of an aeroplane crash $1 \times 10^{-6}$ per year).

**Status:** Concept

**Consideration:** External impact is not included in the failure frequencies for storage vessels. If external impact cannot be excluded, an additional failure frequency should be added. In the Guideline for Quantitative Risk Assessment the value of the additional failure frequency is given only for pressure vessels; this value is very high and is intended to force the establishment to take measures to prevent external impact from traffic.
on the site. For atmospheric tanks the use of an additional failure frequency is not described explicitly.

Since external impact is not included in the failure frequencies, an additional failure frequency should be added for the impact of aeroplanes. However, if the probability of failure due to an aeroplane crash is low (i.e. a factor 10) compared to the standard failure frequencies, the contribution of an aeroplane crash can be neglected.

To determine the contribution of an aeroplane crash to the standard failure frequency, it should be considered how the risk contours of an airport are calculated. For each aeroplane, a crash area is determined. The crash area is equal to 83 m$^2$ per ton MTOW (Maximum Take-Off Weight). It is assumed that within the crash area the probability of death of a person is equal to 0.278. If it is assumed that (1) the area of a tank is small compared to the crash area and (2) the effect of a fragment, leading to death of a person, also leads to failure of the tank, the contribution of an aeroplane crash to the standard failure frequency is in the order of the location-specific risk from aeroplanes at the location of the establishment.

It should be noted that more than one tank can be situated in the crash area. Thus the crash of a large aeroplane may lead to the simultaneous failure of a number of tanks within the crash area. For simplicity, failure of a number of tanks simultaneously due to the aeroplane crash is neglected. For each tank, the location-specific risk of an aeroplane crash is added to the standard catastrophic failure frequency and the frequency is evenly divided in an instantaneous release and a continuous release of the inventory in 10 minutes.

The domino effect that failure of one tank may lead to failure of another tank nearby should be considered in the standard way.

**Question:** A storage tank of an LPG filling station is situated underground. Is a reduction in the failure frequency allowed?

**Answer:** Yes, the scenario BLEVE is excluded. For a storage tank of LPG (more than 10 tonnes) situated underground, the scenarios are:
- instantaneous release to be modelled as an explosion / flash fire ($2.5 \times 10^{-7}$ per year)
- continuous release ($5 \times 10^{-7}$ per year)
- 10 mm hole ($1 \times 10^{-5}$ per year)

Modelling the instantaneous release as an explosion / flash fire is described in another question.

**Status:** Concept

**Consideration:** The Guidelines state on one hand “A lower failure frequency can be used if a tank or vessel has special provisions additional to the standard provisions, e.g. according to the design code, which have an indisputable failure-reducing effect. However, the frequency at which the complete inventory is released (i.e. the sum of the frequencies of the LOCs, G.1 and G.2) should never be less than 10$^{-7}$ per year.” and on the other hand “Vessels and tanks can be (partly) in-ground, or
situated inside or outside a building. The LOCs and their frequencies are not dependent on the situation. The modelling of a release inside a building is described in Chapter 4.”

A storage tank at an LPG filling station is situated underneath a thick layer of soil and a slab of concrete. This situation is considered as a special provision. In this case, a BLEVE of the LPG tank due to a fire underneath the tank or a jet fire is considered impossible. The scenario BLEVE and fireball is therefore excluded.

The reduction in failure frequency depends on the probability of direct ignition and therefore on the amount of material stored. An example of the event trees for storage above ground and storage underground is given in the figures A and B. The amount stored in this example is larger than 10 tonnes, and the probability of direct ignition is therefore 0.7.

**Figure A**  Event tree for the instantaneous release of an LPG storage tank above ground (>10 tonnes)

**Figure B**  Event tree for the instantaneous release of an LPG storage tank underground (>10 tonnes)
Question: A heat exchanger is a tube shell type, with ammonia as cooling medium in the shell. The construction is comparable to a pressure vessel. Is the application of the failure frequencies of a pressure vessel allowed?

Answer: No, the failure frequencies of a heat exchanger should be used.

Status: Concept

Question: Table 3.21 gives the frequencies of LoCs for ships in an establishment. Are the frequencies for the LoCs ‘E.1 - External large spill’ and ‘E.2 - External small spill’ correct?

Answer: The frequencies of E.1 and E.2 are not correct in Table 3.21. The correct values for are:

<table>
<thead>
<tr>
<th>Ship</th>
<th>E.1 External large spill</th>
<th>E.1 External small spill</th>
</tr>
</thead>
<tbody>
<tr>
<td>single-walled liquid tanker</td>
<td>0.1 x f₀</td>
<td>0.2 x f₀</td>
</tr>
<tr>
<td>double-walled liquid tanker</td>
<td>0.0015 x f₀</td>
<td>0.006 x f₀</td>
</tr>
<tr>
<td>gas tanker, semi-gas tanker</td>
<td>0.00012 x f₀</td>
<td>0.025 x f₀</td>
</tr>
</tbody>
</table>

Status: Concept

Question: Table 3.21 gives the standard failure frequency for loading / unloading of a ship. These frequencies are very high with respect to experience in the Rotterdam harbour. Are new, updated failure frequencies available for use in a QRA calculation.

Answer: Yes, it is decided that the failure frequencies for loading / unloading a ship are equal to the failure frequencies for loading / unloading a road tanker or tank wagon. The updated table 3.21 in CPR 18E now reads:

<table>
<thead>
<tr>
<th>Ship</th>
<th>L.1</th>
<th>L.2</th>
<th>E.1</th>
<th>E.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full bore arm</td>
<td>Leak arm</td>
<td>External large spill</td>
<td>External small spill</td>
</tr>
<tr>
<td>Single-walled liquid tanker</td>
<td>3 x 10⁻⁸ per hour</td>
<td>3 x 10⁻⁷ per hour</td>
<td>0.1 f₀</td>
<td>0.2 f₀</td>
</tr>
<tr>
<td>Double-walled liquid tanker</td>
<td>3 x 10⁻⁸ per hour</td>
<td>3 x 10⁻⁷ per hour</td>
<td>0.0015 f₀</td>
<td>0.006 f₀</td>
</tr>
<tr>
<td>Gas tanker, semi-gas tanker</td>
<td>3 x 10⁻⁸ per hour</td>
<td>3 x 10⁻⁷ per hour</td>
<td>0.00012 f₀</td>
<td>0.025 f₀</td>
</tr>
</tbody>
</table>
After study of a number of references (Report of the Rotterdam Harbour Authority, included in the Safety Report of Hydro Agri Sluiskil B.V. TNO rapport R2001/609 version 2; AMINAL. Handboek kanscijfers ten behoeve van het opstellen van een Veiligheidsrapport. Versie 1, 1994;LPG-Integraal; hoofdrapport en deelrapport 1121; TNO. Derivation of failure frequencies for LoC cases. TNO-MEP-R 98/501, 1998) it is decided that the best estimate for the failure frequencies for loading / unloading a ship are equal to the failure frequencies for loading / unloading a road tanker or tank wagon. For a detailed description, see the document: P. Uijt de Haag (RIVM), *Frequentie laad- en losarmen* of November 4, 2002. (Document RE 02-11).

**Modelling of discharge and dispersion**

**Question:** According to the Guidelines: *Where no BLEVE and fire ball occur following an instantaneous release with direct ignition, a vapour cloud expanded to atmospheric pressure and a liquid pool are formed. The direct ignition of the vapour cloud is modelled as a flash fire and explosion. How should this be modelled?*

**Answer:** The flash fire (probability 0.6) should be modelled by expanding the initial cloud to UFL with air entrainment. The damage area corresponds to the UFL cloud footprint. The explosion (probability 0.4) is modelled using the total mass within LFL (in this case equal to UFL).

**Status:** Concept

**Consideration:** Instantaneous failure of a storage tank with pressurised liquefied gas may occur by two different types of processes. The storage tank is heated by irradiation or a chemical run-away reaction. The tank fails at a pressure higher than the storage pressure and direct ignition results in a BLEVE and a fireball. The storage tank fails by external impact or errors in design and construction at storage pressure. A flammable cloud is formed and a liquid pool.

The guidelines prescribe that in case no BLEVE and fireball occur, the flammable cloud expands to atmospheric pressure and direct ignition should be modelled as a flash fire (probability 0.6) and explosion (probability 0.4).

It should be noted that the difference between direct ignition and delayed ignition is indistinct. Direct ignition means: in a short time after failure. An example would be an external impact of a motor-car followed by ignition caused by a hot surface of the same car. In
modelling the flash fire of the flammable cloud, the following considerations were taken into account:

- Ignition can not occur directly at the time of failure, since then a BLEVE and fireball occur.
- Entrainment of air is necessary to result in a flash fire.
- It is not likely that a stoichiometric cloud is formed if the ignition is at a short time interval after failure.
- The expansion of the cloud is upwards, based on (i) video material, (ii) air is entrained from the sides and (iii) the flame speed is relatively low in a flash fire.

Based on these considerations it is proposed to model the flash fire (probability 0.6) as follows:

- The initial cloud expands to UFL with air entrainment.
- After ignition the expansion of the cloud is directed upwards.
- The damage area therefore corresponds to the UFL cloud footprint.

The explosion (probability 0.4) is modelled using the total mass within LFL (in this case equal to UFL).

Direct ignition of a cloud with a concentration at UFL results in lower overpressure compared to ignition of a stoichiometric mixture. It is therefore to be considered to model the situation as a flash fire with probability 1. In an update of the Guidelines this will be carefully thought about.

Question: What is the probability of direct ignition for the scenario ‘rupture of loading hose’ of a tank car?

Answer: For the scenario ‘rupture of loading hose’ of a tank car the ignition probabilities for installations should be used, i.e. dependent on substance and outflow.

Status: Concept

Question: What is the ignition probability of ethylene oxide?

Answer: The ignition probability of ethylene oxide is the ignition probability of a ‘high reactive’ gas.

Status: Concept

Consideration: Ethylene oxide is a substance with a boiling point of 11 °C and a flame point of –57 °C; the substance is ‘high reactive’. The substance is often stored as a liquid at a temperature of 0 – 5 °C. At ambient temperature, 9 °C, ethylene oxide is a liquid.

In the Guidelines a distinction is made in K1-liquid, low reactive gas and average/high reactive gas. The guidelines do not give the definition of what is considered to be a gas or liquid.

The classification of a K1-liquid is part of the classification of liquid oil products. The classification method is as follows:
WMS-class | Boundaries | Class
--- | --- | ---
Extremely flammable | Boiling point < 308 K (35°C); Flame point < 273 K (0°C) | K0
Highly flammable | not K0 and Flame point < 294 K (21°C) | K1
Flammable | 294 K (21°C) < Flame point < 328 K (55°C) | K2
 | 328 K (55°C) < Flame point < 373 K (100°C) | K3
 | 373 K (100°C) < Flame point | K4

Flammable pressurised liquefied gases are classified as K0. For the ignition probabilities, the classification method of oil product will be used. the ignition probabilities are therefore as follows:

<table>
<thead>
<tr>
<th>WMS-class</th>
<th>Class</th>
<th>Ignition probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extremely flammable</td>
<td>K0</td>
<td>Gas (dependent on amount/reactivity)</td>
</tr>
<tr>
<td>Highly flammable</td>
<td>K1</td>
<td>K1-liquid</td>
</tr>
<tr>
<td>Flammable</td>
<td>K2</td>
<td>To be defined</td>
</tr>
<tr>
<td></td>
<td>K3</td>
<td>To be defined</td>
</tr>
<tr>
<td></td>
<td>K4</td>
<td>To be defined</td>
</tr>
</tbody>
</table>

Ethylene oxide is a substance with a boiling point of 11°C and a flame point of –57°C, is therefore a K0-substance and the ignition probability of ethylene oxide is the ignition probability of a ‘high reactive’ gas.

Status: Concept

Question: A hole in a vessel results in a continuous emission. Due to the impulse of the jet, rain-out occurs outside the bund and the model calculates a very large pool. On an industrial site drains, elevations, roads and the like are present, possibly limiting the extent of the pool. Is it possible to consider these type of boundaries to the pool in the QRA.

Answer: Yes

Consideration: In principle, it is possible to consider limitations to the extent of the pool due to platforms, roads, drains and the like. If in all directions barriers are present capable of limiting the pool size, this can be included in the QRA as a large bund. The presence of drains is more complicated. Evaporation of the dangerous substance occurs in the sewer, thus contributing to the cloud. Drains to a sewer can therefore only be considered if the evaporation in the sewer is considered as well. This means that the pool above ground should be combined with an effective pool beneath ground.

Status: Concept

Question: Should a BLEVE of a tanker with ethylene oxide be included in the QRA calculation?
Answer: Yes.

Consideration: Ethylene oxide is a substance with a boiling point of 11°C and a flame point of −57°C; the substance is ‘high reactive’. The substance is often stored as a liquid at a temperature of 0 – 5°C. At ambient temperature, 9°C, ethylene oxide is a liquid. A BLEVE is usually considered for a gas only. In the Purple Book, a distinction is made in K1-liquid, low reactive gas and average/high reactive gas with respect to the ignition probabilities. The Purple Book does not define what is considered to be a gas or K1-liquid.

To define the difference between flammable gases and K1-liquid, we consider the classification of oil products.

<table>
<thead>
<tr>
<th>WMS-class</th>
<th>Boundaries</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extremely flammable</td>
<td>Boiling point &lt; 308 K (35°C); Flame point &lt; 273 K (0°C)</td>
<td>K0</td>
</tr>
<tr>
<td>Highly flammable</td>
<td>not K0 and Flame point &lt; 294 K (21°C)</td>
<td>K1</td>
</tr>
<tr>
<td>Flammable</td>
<td>294 K (21°C) &lt; Flame point &lt; 328 K (55°C)</td>
<td>K2</td>
</tr>
<tr>
<td></td>
<td>328 K (55°C) &lt; Flame point &lt; 373 K (100°C)</td>
<td>K3</td>
</tr>
<tr>
<td></td>
<td>373 K (100°C) &lt; Flame point</td>
<td>K4</td>
</tr>
</tbody>
</table>

Flammable pressurised liquefied gases are classified as K0. It is therefore recommended that all K0 substances are to be considered as ‘gases’ with respect to the ignition probability and the possibility of a BLEVE. Ethylene oxide is a substance with a boiling point of 11°C and a flame point of −57°C and is therefore a K0-substance. It is concluded that a BLEVE of a tanker with ethylene oxide should be included in the QRA.

Status Concept

Question: In the risk calculation of a CPR-15 storage, it is assumed that the (toxic) combustion products are cooled by the building for a time period of 20 - 30 minutes and therefore no plume rise occurs. After this period, plume rise occurs and toxic combustion products are transported upwards. When plume rise occurs, it is assumed that at ground level the concentration of combustion products is not lethal. In the open air, cooling of the plume by the building does not occur. How should the risk of a storage in the open air be calculated?

Answer: If the storage is in the open air, but inside the lee of an adjacent building, the modelling should be according to the risk method of CPR-15, assuming that the combustion products are released in the lee of the building. If the storage is in the open air and the plume will not be trapped in the lee of an adjacent building, plume rise occurs and no lethal effects at ground level are expected.
Consideration: If the storage is in the open air, but inside the lee of an adjacent building, the plume may be trapped in the lee of this building and mixed with colder air. This situation is similar to the release in the lee of a building. It is proposed to model this situation like the release from the intact storage building.

In reality, a large fire in the lee of a building may still give plume rise and the approach suggested here will probably overestimate the risk.

If the storage is in the open air and the plume will not be trapped in the lee of an adjacent building, plume rise will occur. In order to estimate the effects of the plume rise, a test calculation is made with PHAST 6.21. The calculation is done for the sample substance of Section 4.5.2.2 of the Risk analysis method CPR-15, namely $C_{3.28}H_{4.35}O_{1.38}Cl_{1.10}N_{0.23}S_{0.06}$. Various surface areas are used, namely 20 m$^2$, 100 m$^2$ and 400 m$^2$. The burning rate is surface-limited, 0.025 kg m$^{-2}$ s$^{-1}$. The amount of toxic substances in the combustion gases is 0.4332 kg per kg burnt product. For a surface area of 20 m$^2$, the total mass source term is the sum of:

- product, 0.5 kg s$^{-1}$ (= 4.55 moles)
- oxygen, 0.5 kg s$^{-1}$ (3.54 mole O$_2$ per mole product, i.e. $3.54 \times 4.55$ mole s$^{-1}$ × 32 g mole$^{-1}$)
- nitrogen, 1.8 kg s$^{-1}$ (4 mole N$_2$ per mole O$_2$, i.e. $4 \times 3.54 \times 4.55$ mole s$^{-1}$ × 28 g mole$^{-1}$)

The source term thus adds up to 2.8 kg/s combustion gases with 0.22 kg/s toxic combustion products (fraction 0.077).

Dispersion calculations are made for different combinations of temperature and surface area for two weather classes, D5 and F1.5. Nitric oxide is selected as sample substance; the molecular mass of nitric oxide (30) is slightly higher than the molecular mass of air (29) and thus any plume rise is caused by temperature differences and not by differences in molecular mass. According to Section 4.5.2.2 of the Risk analysis method CPR-15, the 1% lethality concentration of the toxic combustion products is between 461 – 1224 mg/m$^3$ for an exposure period of 10 – 30 minutes. Using a density of 1.25 kg/m$^3$ for the cloud and a fraction of toxic combustion products of 0.077, the concentration of combustion gases corresponding to 1% lethality is 4800 – 12700 ppm.

Calculation results are shown in the table, i.e. the distance corresponding to a concentration of combustion gases of 10 000 ppm (approximately 1% lethality) at ground level (1 m). The temperature of 10 ºC is the reference situation where no plume rise occurs.

<table>
<thead>
<tr>
<th>Source term</th>
<th>D5 10 000 ppm</th>
<th>F1.5 10 000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8 kg s$^{-1}$ combustion gases at 10 ºC</td>
<td>30 m</td>
<td>110 m</td>
</tr>
<tr>
<td>2.8 kg s$^{-1}$ combustion gases at 100 ºC</td>
<td>12 m</td>
<td>no hazard</td>
</tr>
<tr>
<td>2.8 kg s$^{-1}$ combustion gases at 200 ºC</td>
<td>12 m</td>
<td>no hazard</td>
</tr>
<tr>
<td>2.8 kg s$^{-1}$ combustion gases at 300 ºC</td>
<td>10 m</td>
<td>no hazard</td>
</tr>
<tr>
<td>14 kg/s combustion gases at 10 ºC</td>
<td>70 m</td>
<td>460 m</td>
</tr>
</tbody>
</table>
The calculations show that if the temperature is high, the risk is considerably reduced by the plume rise.

### Other questions

**Question:** Appendix 6.B: is the value of $z = 10.3$ m (page 6.24) correct?

**Answer:** No. The correct value is $z = 23.7$ m.

**Consideration:** The averaging time for toxic substances is 600 s. The fire brigade requires the distances to the concentrations corresponding to intervention levels. For this calculation, should I use an averaging time for toxic substances of 600 s or 3600 s?

**Answer:** 3600 s.

**Consideration:** The averaging time of 600 s is based on the average release durations in the QRA (instantaneous/10 minutes release/ maximum 30 minutes). In the QRA, the calculation is directed at lethality, i.e. high concentrations and an exposure relatively nearby, so that the along-wind dispersion is limited. Intervention levels are based on an exposure time of one hour. Especially the lowest intervention level corresponds to a low concentration and thus far distances and long transport times. Since the exposure time is based on one hour, an averaging time of one hour is reasonable.