Reliable Risk Estimation in the Risk Analysis of Chemical Industry Case Study: Ammonia Storage Pressurized Spherical Tank*

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This paper presents a general overview of a procedure for the evaluation of individual and societal risk connected with accidental release of toxic and/or flammable substances. In this study, methodology and procedure for a probabilistic safety assessment are outlined. Evaluation of individual and societal risk is the key point of the probabilistic safety assessment in chemical industry. The steps of the presented procedure were applied to a pressurized spherical tank for ammonia storage in order to estimate reliable risk of its casual rupture with different magnitude of the tank damage. The case study results demonstrate that further development in the probabilistic safety analysis of chemical industries has to be done, in order to develop more effective and rapid procedures for complex risk estimation with reliable and realistic values of probabilities.

Though safety has always been a critical issue in the design and operation of chemical plants, unfortunately the academic community overlooked this issue for a very long time. The occurrence of catastrophic accidents such as Seveso in 1976, Bhopal in 1984, Flixborough in 1974, Piper Alpha in 1988, Longford in 1998 [1] resulted in lower public acceptance of chemical industry and led to a development of new safety standards and regulations, such as the European directive SEVESO II [2], the OSHA standards [3] for the management of highly hazardous chemicals in the USA, or the Act 261 Standards [4] for prevention of major industrial accidents in Slovakia. It is now essential for chemical companies to carry out systematic analyses in order to convince regulatory agencies and the general public that their technologies are safe.

Important in the first phase of the risk evaluation of any chemical process is the hazard identification. Different techniques for qualitative hazard identification are widely used in chemical industries. The most frequently What-If, Checklists, Preliminary hazard analysis (PHA), and Hazard and operability studies (HAZOP) [5] are applied. The main objectives in the hazard identification step of the risk evaluation are completeness, consistency, and correctness. A satisfactory level of hazard identification for the whole chemical process will be obtained by a combination of several techniques. Indications when and how each of mentioned techniques is applicable are given in [5].

The major disadvantage of the hazard identification techniques is that they are based on mostly qualitative information, which does not represent the complexity of chemical processes. Often, they are effective in identifying potential hazards, still it is usually difficult to determine whether and how these potential hazards actually occur. A realistic understanding of hazards associated with identification of the initiating event would be based on all known information on the process, including quantitative models. Such an approach would facilitate the consideration of the interactions of possible events and quantitative risk analysis has to be applied.

Quantitative risk analysis is used to help evaluate potential risks when qualitative techniques cannot provide adequate understanding of the risks and more information is needed. The basic principle of quantitative risk analysis is to identify incident scenarios and evaluate the risk by defining the probability of failure, and also probability and potential impact of various consequences. The important stages in the quantitative risk analysis are the risk analysis and the risk assessment.

Risk Analysis

When determining potential event sequences and potential incidents, the quantitative risk analysis follows from the qualitative hazard identification. The

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main sources of potential release of hazardous substances are identified and the initiating events that can cause such releases are determined. A complex analysis is normally based on full range of possible incidents for all sources.

Incident consequences analysis consists of definition of a correct source model and dispersion model for hazardous substances, and quantitative estimation of consequences of vapour cloud explosion, flash fire, pool fires, jet fires, BLEVE (boiling liquid expanding vapour explosion), fireball, *etc.* [6, 7].

Potential incident frequency is estimated by means of fault trees or databases for the initial event sequences. Event trees can be used to account for mitigation and post-release events [6, 7]. System failures are in turn modelled in terms of basic component failures and human errors to identify their basic causes and to allow for quantification of the system failure probabilities and accident sequence frequencies.

Further, the effect models are used to estimate the incident (dispersion of toxic hazardous substances, vapour cloud explosion, flash fire, pool fires, jet fires, BLEVE, and fireball) impacts on people, environment, and property. The effect models are developed for toxic gas effects, thermal effects, and explosion effects.

Finally, the risk is estimated assuming all events as a combination of potential consequences for each event with its corresponding event frequency.

Risk Assessment

This stage identifies the major sources of risk and determines whether there are cost-effective processes for the risk reduction. In order to evaluate a risk assessment it is necessary to have appropriate risk criteria.

If the risk is considered to be excessive, the potential risk reduction measures are identified and prioritized.

Measure of Risk

As mentioned above, during the quantitative risk analysis the risk estimation has to be done. A number of different measures of risk can be derived from the same set of incident frequency and consequence data. Most commonly, individual and societal risks are used for the risk characterization.

Individual risk refers to the risk to a person in the vicinity of hazard. This measure includes the nature of the damage to the individual, the likelihood of this damage occurring and the time period over which this damage might occur. There is an individual fatality risk if the damage refers to the death of a person. Individual fatality risk is defined as the frequency with which an individual at a specific location (x, y) relative to the installation(s) will die as a result of an accident in the installation [7].

Individual fatality risk is usually expressed per unit of time (*e.g.* per year) of installation operation. Individual fatality risk at a specific location (x, y) can be calculated from the following equation

$$\mathrm{IR}(x,y) = \sum_{\mathrm{io}=1}^{\mathrm{IO}} P_{\mathrm{io}}(x,y) f_{\mathrm{io}} \qquad (1)$$

where $P_{\mathrm{io}}(x,y)$ is the conditional probability of fatality for an individual at a specific location (x, y) at given incident outcome case *io*, IO is the total number of incident outcome cases considered in the analysis. The frequency of incident outcome case *io*, f_{io}, is obtained by frequency analysis as follows

$$f_{\mathrm{io}} = \sum_{d=1}^{D} f_d P_{\mathrm{io},d} \qquad (2)$$

where $P_{\mathrm{io},d}$ is the conditional probability that the plant damage state case d will lead to the incident outcome case *io*, D is the total number of possible plant damage states. The frequency of the plat damage case d can be obtained by the equation

$$f_d = \sum_{i=1}^{I} f_i P_{d,i} \qquad (3)$$

where $P_{d,i}$ is the conditional probability that the initiating event case i will lead to the plant damage case d, I is the total number of initiating events and f_i is the frequency of the initiating event case i. Finally, individual fatality risk at a specific location (x, y) can be written by combining eqns (*1—3*)

$$\mathrm{IR}(x,y) = \sum_{\mathrm{io}=1}^{\mathrm{IO}} P_{\mathrm{io}}(x,y) \sum_{d=1}^{D} P_{\mathrm{io},d} \sum_{i=1}^{I} P_{d,i} f_i \qquad (4)$$

The conditional probabilities $P_{d,i}$, $P_{\mathrm{io},d}$ and frequencies f_i are calculated in the step "Evaluate the event consequences" of risk analysis or frequencies f_{io} can be directly estimated from a historical database. It should also be noted that the frequencies f_{io} have to be corrected by the wind direction and the angle enclosed by the effect zone. An event tree is commonly used to evaluate these relationships.

Probability $P_{\mathrm{io}}(x,y)$ is calculated during the consequences estimation in the risk analysis based on the dose-response model [8, 9] and dispersion models. The dose-response model calculates the fatality probability for an individual receiving the dose calculated by the so-called probit functions. Probability $P_{\mathrm{io}}(x,y)$ based on probit functions can be written as follows

$$P_{\mathrm{io}}(x,y) = 0.5\left[1 + \frac{P-5}{|P-5|}\,\mathrm{erf}\left(\frac{|P-5|}{\sqrt{2}}\right)\right] \qquad (5)$$

where P is the probit value for fatalities as a result of toxic, thermal or explosion effects. The probit value, P, for the toxic, thermal, and pressure effects can be obtained from the probit equation

$$P = A + B \ln d_{\mathrm{io}}(x, y) \tag{6}$$

where A, B are parameters depending on the incident impacts (toxic, thermal, and pressure effects) and $d_{\mathrm{io}}(x, y)$ is the dose received by the individual calculated by the equation

$$d_{\mathrm{io}}(x, y) = \int_{\mathrm{o}}^{T} f[c_{\mathrm{io}}(x, y, t)]\mathrm{d}t \tag{7}$$

$c_{\mathrm{io}}(x, y, t)$ being the intensity of the incident outcome case *io* effect (*e.g.* concentration of toxic material, heat radiation, overpressure) at point (x, y) and time t is an exposed time at point (x, y). Usually, individual risk is expressed in terms of iso-risk as a curve, that is the locus of points with the same level of individual risk. Also the individual risk can be obtained as a function of the distance from the origin of the accident event according to the equation [8, 10]

$$\mathrm{IR}(x) = \max_{y} \{\mathrm{IR}(x, y)\} \tag{8}$$

On the other hand, this type of expression can be confusing because in most cases there is a group of persons involved in the potential accident, and all of them are exposed to the same level of risk. For example, an individual risk of 0.01 year^{-1} (eqn (*4*)) could mean 100 accident scenarios with 1 fatality consequence or 10000 accident scenarios from which 1 accident case is accompanied with 100 fatality consequences.

To avoid this confusion an additional measure, societal or group risk is used. Societal risk is the risk confronted by a group of persons affected by the accident expressed as the relationship between the frequencies with which the number of fatalities is expected and the number of fatalities exceeding N resulting from incident outcome cases. The result is a set of frequencies as a function of the number of fatalities, plotted as the F—N curve. The total number of people that will die in area A due to the incident outcome *io* can be defined as

$$N_{\mathrm{io}} = \sum_{A} P_{\mathrm{io}}(x, y) h(x, y) \tag{9}$$

where $h(x, y)$ is the number of people at location (x, y) (population density). This process results in IO numbers of N_{io} fatalities, each one associated with one incident outcome. The number of people affected by the total number of incident outcome cases IO has to be determined. It means that for every incident outcome a frequency and the number of people affected has to be recorded. Then, this information is put in a complementary cumulative distribution function

$$F(N) = \sum_{d=1}^{D} f_d P_d(N) \tag{10}$$

where $P_d(N)$ is probability that the plant damage d will result in more than N fatalities and $F(N)$ is the frequency with which an accident is causing N or more fatalities.

The societal risk calculation can be very time-consuming, because fatalities have to be estimated for every incident outcome case. Incidents must be distributed into incident outcomes and incident outcomes cases to evaluate each weather condition, wind direction, and population case. This crucial issue focuses a lot of interest about rapid calculation of societal risk [11—14].

EXAMPLE

The subject for estimation of individual and societal risk is an ammonia pressurized storage tank, together with associated pipelines. The spherical tank has a volume of 1000 m^3, with a designed pressure of 1.5 MPa and a maximum working pressure of 1.2 MPa. In this case study, an average ambient temperature of 15 ℃ and equilibrium pressure in the tank were assumed. The inventory of the sphere has been taken as 555 600 kg (it is 90 % of the maximum capacity). The associated pipelines of 100-mm diameter have been assumed.

RESULTS AND DISCUSSION

During qualitative hazard identification of the pressurized spherical tank for ammonia storage, six unwanted incident outcomes (the plant damage cases $d = 6$) were identified by the HAZOP study. The incident outcomes are summarized in Table 1.

The potential event sequences and incident outcomes for ammonia release are depicted in Fig. 1. Principally, two incident outcome cases of ammonia release, *i.e.* IO = 2, namely toxic dispersion and UVCE (unconfined vapour cloud explosion), were identified through several event sequences.

Heavy gas box model [6] was used to calculate the ammonia dispersion for two atmospheric stability classes F and C, characterized by the wind speed of 1.5 m s^{-1} and 3 m s^{-1}, respectively. The results of consequence analysis of the incident outcome cases for the atmospheric stability class F are summarized in Table 2. Similar results were obtained for the second atmospheric stability class, C.

The incident outcome frequencies and the incident outcome cases UVCE and toxic dispersion are summarized in Table 3. In the case of incident outcomes

Table 1. Incident Outcomes for Pressurized Spherical Tank for Ammonia Storage as Identified by HAZOP

I	Catastrophic failure/rupture of the spherical tank
II	A major crack in the sphere shell, equivalent to a hypothetical hole with a diameter of 50 mm
III	Full bore fracture of a bottom connection on the sphere in front of the valve
IV	Full bore fracture of the relief valve on the sphere
V	Full bore fracture of the pipeline with a diameter of 100 mm for liquid ammonia
VI	Small liquid leakage from the pipeline, equivalent to 10 % of the pipeline diameter hole

Table 2. Consequences Analysis of the Incident Outcome Cases for Atmospheric Stability Class F

Incident outcome	Toxic dispersion			UVCE		
	t/min	LC_{50}/ppm	x/m	m_e/kg	m_{TNT}/kg	x/m
I	60	5626	3500	298648	17578	122
II	60	5626	313	18780	1105	48
III	60	5626	690	73677	4336	76
IV	10	11521	342	6725	396	34
V	30	7424	312	11870	698	41
VI	10	11521	28	69	4	7

t – time of release, LC_{50} – lethal concentration with 50 % mortality during exposition period, x – distance from the source, m_e – amount of ammonia cloud in explosion limit, m_{TNT} – TNT equivalent.

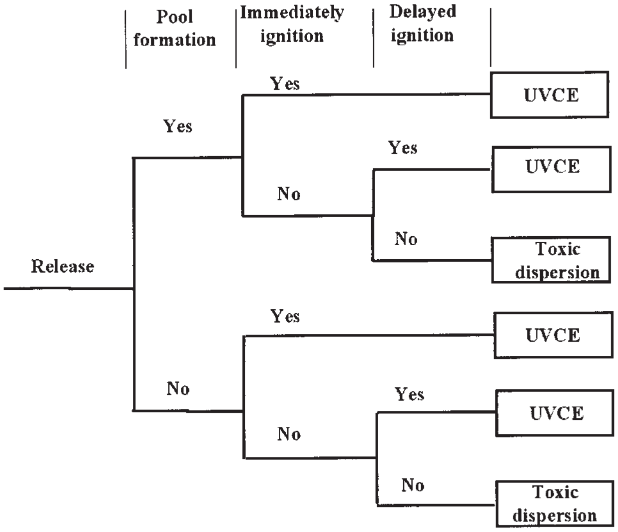

Fig. 1. Potential event sequences and incident outcomes for ammonia release from the pressurized spherical tank.

II—VI, the basic frequencies of the plant damage, f_d, are used from database [6, 15]. Frequency for the incident outcome case I was unknown and for this reason it was calculated by fault tree analysis (Fig. 2). The probit eqn (*6*) for the toxic effects of ammonia can be written as follows

$$Pr = -35.9 + 1.85 \ln\{C^2 t\} \qquad (11)$$

where C/ppm is the concentration of ammonia in the atmosphere. For calculation of received dose using eqn (*7*), the moment of ammonia release corresponded to the zero exposition time.

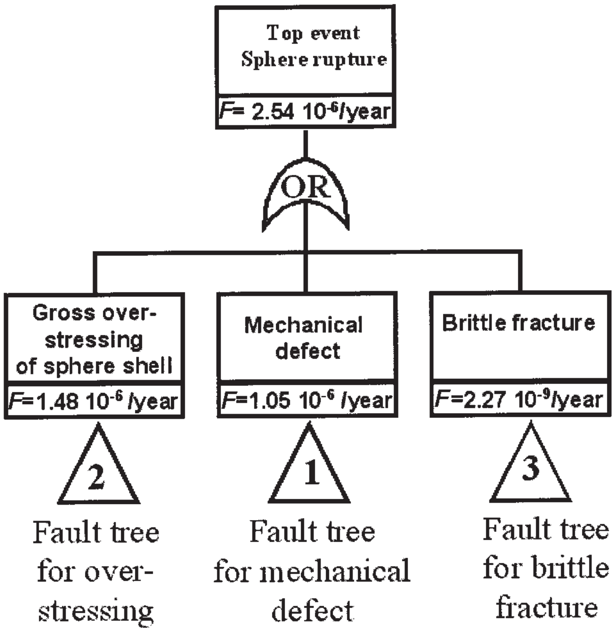

Fig. 2. A part of fault tree analysis for catastrophic rupture of a spherical pressurized tank.

Demonstration of the incident outcome case frequencies by the event tree analysis is depicted in Fig. 3. In the case of catastrophic rupture of the tank sphere, a pool formation is very probable because of a high amount of ammonia released from the damaged tank. According to the enthalpy balance, most of the released ammonia immediately after the incident remains in the liquid state (93 %), meanwhile 7 % evaporates due to the pressure decrease. Probabilities of immediate and delayed ig-

Table 3. Frequencies for the Incident Outcomes and the Incident Outcome Cases

Incident outcome	f_{IO}/year^{-1}	f_{TD}/year^{-1}	f_{UVCE}/year^{-1}
I	2.5×10^{-6}	2.1×10^{-6}	4.8×10^{-7}
II	1.0×10^{-5}	8.1×10^{-6}	1.9×10^{-6}
III	4.2×10^{-6}	3.4×10^{-6}	8.0×10^{-7}
IV	8.7×10^{-5}	7.0×10^{-5}	1.6×10^{-5}
V	7.7×10^{-7}	6.2×10^{-7}	1.5×10^{-7}
VI	1.0×10^{-4}	8.1×10^{-5}	1.9×10^{-5}

IO – incident outcome, f_{IO} – frequency of incident outcome, f_{TD} – frequency of incident outcome case – toxic dispersion, f_{UVCE} – frequency of incident outcome case – UVCE.

nition of formed ammonia pool were assumed [6, 15]. It is clear that the frequencies of incident outcome cases depend strongly on the quality of expert guess or the quality of historical databases of accidents.

Incident outcome cases frequency corrected for different atmospheric classes together with the incident impacts are shown in Table 4. These frequencies are used for individual risk calculation by eqn (*1*). It should be noted that for the individual risk calculation mortality of 100 % for all persons within the affected area defined by the LC_{50} concentration was assumed; thus, $P_{\mathrm{io}}(x, y) = 1$.

The maximum individual risk defined by eqn (*8*) as a function of the downwind distance x from the spher-

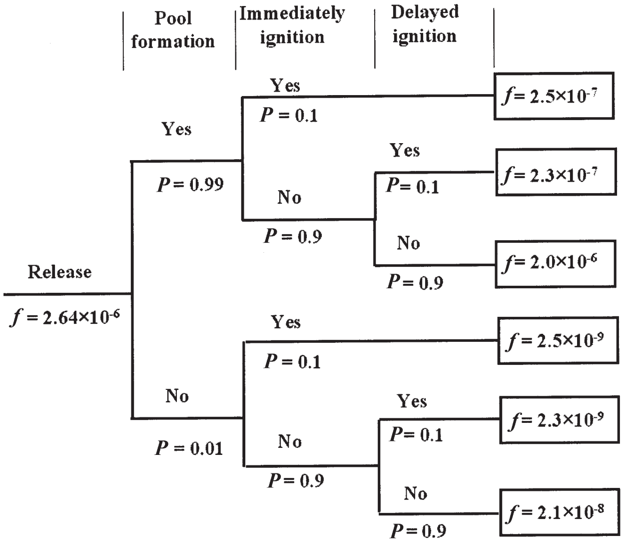

Fig. 3. Incident outcome cases frequency calculation by the event tree analysis for incident outcome I.

Table 4. Incident Outcome Cases Frequencies Corrected for an Atmospheric Class and the Incident Impacts

Incident outcome	Incident outcome case	Atmosphere stability	w/(m s^{-1})	f_{IO}/year^{-1}	x/m
I	UVCE	F	1.5	3.7×10^{-7}	647
		C	3.0	9.4×10^{-8}	1075
	Toxic dispersion	F	1.5	1.6×10^{-6}	3500
		C	3.0	4.0×10^{-7}	3600
II	UVCE	F	1.5	1.5×10^{-6}	110
		C	3.0	3.7×10^{-7}	74
	Toxic dispersion	F	1.5	6.2×10^{-6}	313
		C	3.0	1.6×10^{-6}	443
III	UVCE	F	1.5	6.1×10^{-7}	208
		C	3.0	1.6×10^{-7}	134
	Toxic dispersion	F	1.5	2.6×10^{-6}	690
		C	3.0	6.7×10^{-7}	966
IV	UVCE	F	1.5	1.3×10^{-5}	129
		C	3.0	3.2×10^{-6}	75
	Toxic dispersion	F	1.5	5.4×10^{-5}	342
		C	3.0	1.4×10^{-5}	476
V	UVCE	F	1.5	1.1×10^{-7}	113
		C	3.0	2.9×10^{-8}	72
	Toxic dispersion	F	1.5	4.8×10^{-7}	312
		C	3.0	1.2×10^{-7}	441
VI	UVCE	F	1.5	1.5×10^{-5}	18
		C	3.0	3.7×10^{-6}	18
	Toxic dispersion	F	1.5	6.2×10^{-5}	28
		C	3.0	1.6×10^{-5}	41

w – wind speed, f_{IO} - frequency of incident outcome, x – distance from the source where LC_{50} concentration is reached.

Table 5. Number of Fatalities Due to the Incident Outcome Case Toxic Dispersion for Incident I and the Atmospheric Class F

Wind direction	f_i/year^{-1}	Affected area company/city	Number of people in the affected area		
			Company	City	Sum
N	2.0×10^{-7}	Y / N	1527	–	1527
NE	2.0×10^{-7}	Y / N	1726	–	1726
E	2.0×10^{-7}	Y / N	1527	–	1527
SE	2.0×10^{-7}	Y / N	863	–	863
S	2.0×10^{-7}	Y / Y	199	8000	8199
SW	2.0×10^{-7}	N / Y	–	5000	5000
W	2.0×10^{-7}	Y / Y	199	8000	8199
NW	2.0×10^{-7}	Y / N	863	–	863

f_i – frequency of the incident outcome case toxic dispersion for incident I.

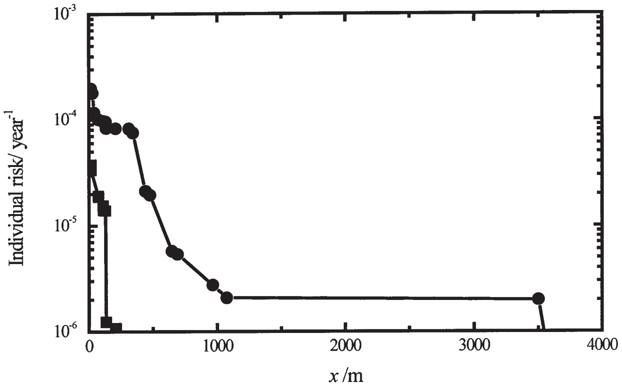

Fig. 4. Maximum individual risk. ● Toxic dispersion and UVCE, ■ UVCE only.

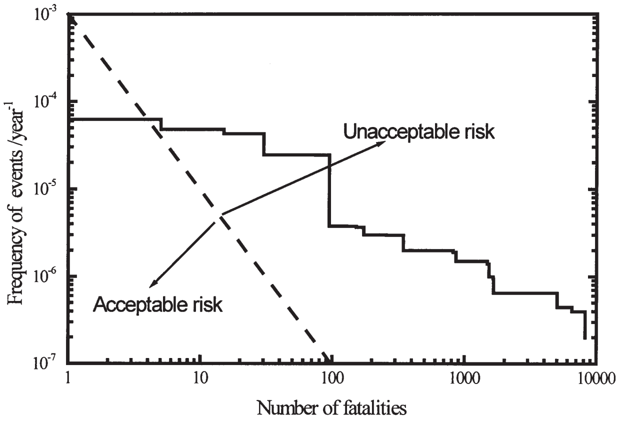

Fig. 5. Societal risk F—N curve (solid line) and the risk acceptability limit value (dashed line) for the ammonia spherical tank.

ical tank is given in Fig. 4. At a zero distance, the value of maximum individual risk is 2×10^{-4} year^{-1} largely exceeding the limit value of 1×10^{-5} year^{-1}. It means that level of the individual risk is unacceptable and further safety action has to be done for the spherical tank. Furthermore, the most important contribution to the individual risk is the toxic dispersion. Incident outcome case, UVCE, contributes to the individual risk only in the close vicinity of the explosion epicentre.

Table 6. Number of Fatalities Due to Incident Outcome Case UVCE for Incident I and the Atmospheric Class F

Wind direction	f_i/year^{-1}	Affected area company	Number of people in the affected area
N	4.6×10^{-8}	Y	152
NE	4.6×10^{-8}	Y	152
E	4.6×10^{-8}	Y	15
SE	4.6×10^{-8}	Y	76
S	4.6×10^{-8}	N	–
SW	4.6×10^{-8}	N	–
W	4.6×10^{-8}	N	–
NW	4.6×10^{-8}	Y	76

f_i – frequency of the incident outcome case toxic dispersion for incident I.

Societal risk calculation requires an estimate of the number of people deceased due to each incident outcome case. For this example the wind direction is divided into an 8-point wind rose. A city with the population density of 20 persons per 10000 m^2 situated 2.5 km far from the spherical tank was considered. A company area of 2.65 km^2 and the corresponding population density of 10 persons per 10000 m^2 were assumed. The number of fatalities due to the incident outcome cases toxic dispersion and UVCE for incident I for the atmospheric class F are summarized in Tables 5 and 6, respectively. The number of fatalities was calculated by eqn (*9*).

The same procedure was applied for the remaining incident outcomes II—VI. Finally, the societal risk F—N curve for the ammonia spherical tank was obtained by applying eqn (*10*) to the number of fatalities. In Fig. 5 the F—N curve exceeds the dashed line corresponding to the limit of unacceptable risk. Therefore, also societal risk is too high, as in the case of the individual risk, and the corresponding safety measures should be adopted.

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