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Assessment of Risk Zones in A Seveso Plant: A Case Study

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Abstract: The assessment of the consequences of industrial accidents takes on a significant interest in the risk analysis of a “Seveso” plant. In fact the estimate of risk zones extent represents a basic element for the characterization of accident scenarios and for the definition of the outcomes to include in the Safety Report, which is mandatory for Seveso plants. In this paper, a case study, referred to a release of a toxic gas liquefied under pressure (anhydrous ammonia), is illustrated. This choice depends on massive ammonia use in several industrial processes. In many cases, when a gas liquefied under pressure is released, aerosol formation is predominant and often causes that all spilled liquid flow forms the gaseous cloud without generating the puddle (two-phase release). Aerosol presence increases vapor mass in the cloud and its density. It follows that gases, which usually should be lighter than air, act as heavy gases. In the paper, effect of toxic release (top event) on human health has been determined by the risk zones extent calculation, which has been performed by a specific software (Effects).

Key words: liquefied ammonia, Seveso plant, atmospheric stability class, risk zones

1. Introduction

The evaluation of the consequences of industrial accidents takes on a significant interest in the risk analysis of a “Seveso” plant. Indeed the estimate of risk areas extent represents a basic element for the characterization of accident (top event) scenarios and for the definition of the outcomes to include in the Safety Report [1], which is compulsory for the plants subjected to Seveso Directive. Furthermore it is obvious the significance of these evaluations both for the arrangement of the internal and external Emergency Plan and for land-use planning. The size of risk areas, deriving from a dangerous substance release, can be only assessed on the base of a modelling, which considers simplified hypotheses, which introduce an unavoidable degree of uncertainty due to the intrinsic nature of accidental event. Indeed, it is only possible to appraise some factors, that determine the major effects (geometrical features of the release in environment, thermodynamic parameters of the emitted substance, incomplete representation of chemical-physical events described in the adopted simulation model, etc.). In this paper, a toxic release in a Seveso plant has been investigated. A storage of anhydrous ammonia has been selected, as it constitutes a common situation for several Seveso plants. In fact ammonia is widely used in the process industry mainly for fertilizers production. In addition to this usage, ammonia is used in explosives production, manufacturing of metals, petroleum refining and other chemicals production processes as well as a refrigerant. Due to its massive use, ammonia is often involved in accidents. In particular ammonia is one of the main substances, which have been rather often involved in accidents notified to the Commission of the European Community under the

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requirements of the Seveso Directive. Anhydrous ammonia has been frequently reported for accidents, causing death/injury and evacuation. The paper has been focused on risk zones appraisal with reference to actual regulations for that concerns the leakage of a toxic substance from a Seveso plant in order to assess the effects of the accident on health of workers and population, living nearby the plant. The estimate of risk zones is mandatory for "Seveso" plants and must be reported in Safety Report. The release of anhydrous ammonia and the extent of risk zones have been investigated by a specific software Effects, produced by TNO. The atmospheric stability classes D5 and F2 have been examined to assess the influence of meteorological parameters on toxic cloud dispersion.

2. Material and Methods

A reliable risk analysis of major hazards is essential as a support to the emergency management and the development of land use planning [2], aimed at reducing the impact on the surrounding territory and therefore the consequences on human health and environment. This analysis requires the identification of possible failures in industrial plant elements, which can produce the emission of a dangerous substance, the frequencies of occurrence, the appraisal of accident scenarios and the evaluation of the consequences described in risk zones, where the effects, induced by accident, exceed a predetermined threshold value, in terms of damage for mankind, land and structures. The release of liquefied ammonia and extent of risk zones have been investigated by Effects, which is able to assist in performing safety analysis for the process industry. The extent of risk areas is referred to concentrations, which are established by the Guidelines of Italian Civil Protection Department [3] for toxic compounds. In this paper the zones, exposed to different risks, are described with reference to an anhydrous ammonia emission, as follows:

- First Zone: Maximum Exposure Zone (high lethality). This is an area in the immediate vicinity of the factory and is generally exposed to serious effects on health (death);
- Second Zone: Damage Zone (irreversible damage). This is a zone where consequences of an accident are still serious, particularly for some categories at risk (children, elderly or ill people, pregnant women);
- Third zone: Caution Zone. This is the furthest zone from an accident, where effects are not generally serious.

For the definition of the zones as defined above, in case of a toxic emission, the following reference values have been considered:

- First zone: LC_{50} (lethal concentration 50). It is a standard measure of the toxicity of the surrounding medium, that will kill half of the sample population of a specific test-animal in a specified period through exposure via inhalation (respiration);
- Second zone: IDLH (immediately dangerous to life and health);
- Third zone: IDLH/10.

Anhydrous ammonia (a toxic gas liquefied under pressure) is stored at a temperature much higher than its normal boiling temperature ($T_{B_{NH_3}} = 240.15 K$) and therefore it undergoes a rapid initial vaporization (flashing) after release, whereby the generated vapor breaks up the liquid into a fine spray of droplets [4], which are sufficiently small that no significant rain-out onto the ground is observed. These storage conditions generate a release of a two-phase mixture, where aerosol presence can be very high. In these cases it follows that ammonia cloud can be classified as a dense gas. The release of liquefied ammonia has been studied by TPDIS (Two-Phase discharge of liquefied gases through a pipe) Model, which allows to appreciate the influence of gravity on two-phase flow and to include a more detailed description of the flow friction at pipe walls. Such model is aimed at predicting the mass flow rate, the velocity, the mass fraction of vapour and the thermodynamic state of the outflowed fluid as a function of the initial conditions.

3. The Case Study: The Plant and Its Anhydrous Ammonia Storage

The plant is located in an Italian industrial area and shares common services such as utilities, gate guards, a fire brigade, first aid and canteen with several chemical compounds. The site has two main production units: an ammonia and urea plant. Ammonia production is based on natural gas, supplied via an adjacent pipeline. About sixty percent of the ammonia is directly used in the urea plant and the remainder is sent via pipeline or sold to industrial customers via train or truck. Anhydrous ammonia is stored in horizontal cylindrical tanks (Fig. 1), rated for 18 bar. Volume of these tanks is equal to 25 m^3 and their maximum percentage of filling (per volume) is equal to 85%. Ammonia storage conditions are:

- 293.15 K (storage temperature);
- 8.6 bar (storage pressure).

The plant is subject to Seveso Directive and in particular, the paper has been focused on assessment of outcomes of an accident (top event), deriving from anhydrous ammonia (toxic compound) release, generated by a transfer pump leakage.

4. Emission of Anhydrous Ammonia: Accident Hypothesis

According to the Regulation (EC) 1272/2008, anhydrous ammonia belongs to the third category of acute toxicity and category code 1 B, referred to skin corrosion [5]. Hazard statement codes, which are related to the previous categories, respectively are H 331 and H 314. Anhydrous ammonia is a toxic liquefied gas typically stored in pressure vessels and there are significant risks and liabilities associated with its transport, unloading and storage. In the present paper, accident, which could generate anhydrous ammonia emission and the consequent formation of toxic cloud, derives from a transfer pump failure (continuous release). Such failure is considered as a loss of containment event (LOC) and its frequency is about 2.5×10^{-4} events/year [6]. Releases from pumps depend on seals losses, which can be caused by:

- seal breakage;
- pipes connected with the pump;
- insufficient lubrication;
- vibrations due to defective bearings, cavitation and wrong pump installation.

Assumed parameters for studying atmospheric ammonia dispersion and estimating the extent of risk areas have been:

- hole diameter (D_h);
- stored anhydrous ammonia pressure and temperature;
- meteorological conditions (Pasquill stability classes).

Ammonia pipe diameter is equal to 80 mm, while hole diameter, used for the analysis, is equal to 10% (D_h = 0.008 m) of the nominal diameter as indicated by the Purple Book [6]. Pipe, which connects liquified ammonia storage tank with transfer pump, is 1.2 m long. Consequences assessment of exposure to toxic compound (anhydrous ammonia) has been carried out in accordance with atmospheric stability classes (D5 characterized by neutral conditions and v_{wind} = 5 m/s and F2, characterized by moderately stable conditions and v_{wind} = 2 m/s), which are reported in Decree, issued by Italian Civil Protection Department and referred to “Planning of external emergency”. In

Fig. 1 Anhydrous ammonia storage tanks.

accordance with this regulation the following thresholds have been used:

LC_{50} = 3,000 ppm (2,280 mg/m^3);

IDLH = 300 ppm (228 mg/m^3);

IDLH/10 = 30 ppm (≅23 mg/m^3).

Examining meteorological data [7] of industrial site, it has been assumed that the wind blows from the north-east (Fig. 2).

5. Air Dispersion of Toxic Cloud

The accidental emission of a volatile chemical can be a threat to life and health even far from the point of origin. Air dispersion models are basic to predict hazard zones associated with toxic or flammable gas clouds and therefore how their concentration varies with distance. As anhydrous ammonia is stored as a gas liquefied under pressure above its boiling temperature, a two-phase release scenario occurs. During the liquid ammonia emission, a fraction (m_{vap}) flashes, a share ($m_{aerosol}$) forms an aerosol and a small part ($m_{rain\text{-}out}$) rains out to form a puddle.

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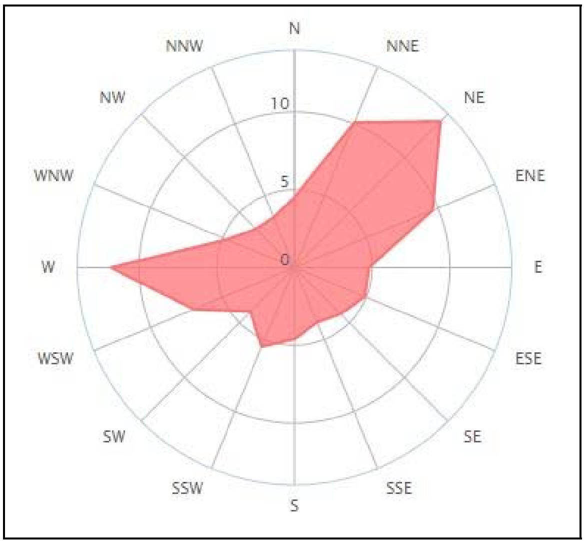

Fig. 2 Wind (industrial site): annual average direction distribution.

cloud and its density both for droplets presence and for temperature decrease due to liquid vaporization [8]. It follows those gases, which usually should be lighter than air (molecular weight of ammonia is lower than that of air), act as heavy gases. Ammonia dispersion and the consequent estimate of risk areas extent consist of two distinct steps:

1) calculation of released mass flow (release of liquefied ammonia);

2) study of toxic cloud dispersion (dense gas dispersion).

These two steps have been carried out and simulated by Effects. Output of the first step constitutes, together with meteorological conditions and terrain roughness, an input for predicting ammonia concentration distribution. Releases of dense gas introduce some special effects, which affect the dispersion. The released compound will descend to the surface and, once on the ground, spread radially under influence of the gravitational forces. This self-induced flow produces a shallow cloud with increased horizontal extent. At the front of the so-called "gravity current" a head will develop with a strong vorticity (Fig. 3). This velocity field is deterministic in nature and will replace, for the duration of the gravity spreading, the random atmospheric turbulence [9]. The self-induced flow will increase mixing, especially just behind the gravity head. After gravity spreading has finished, the vertical variation of density in the cloud will cause a stable stratification in the cloud, which reduces dispersion in vertical direction [10]. Finally, the effects of density will be dispersed and negligible and dispersion will become passive [11]. The significant quantity of aerosol makes cloud heavy and an efficient air dilution only allows the passage from heavy gas to neutral gas.

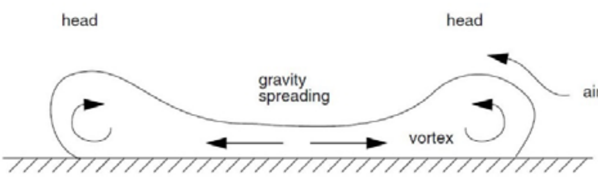

Fig. 3 Gravity spreading of a dense gas cloud.

In Table 1 selected parameters, assumed for studying ammonia outflow and predicting its concentration distribution, are shown.

Table 1 Selected parameters for the case study.

	Parameter	Value
Pipe	Diameter	0.08 m
	Length	1.2 m
	Roughness	0.045 mm
Anhydrous ammonia tank	Volume	25 m^3
	Percentage of filling (per volume)	85%
Operating conditions	Ammonia pressure	8.6 bar
	Ammonia temperature	293.15 K
Accident hypothesis	D_h (leakage from pump)	0.008 m
Ammonia outflow	Release duration	600 s
	Discharge coefficient	0.7
Terrain	Roughness	0.1 m
Meteorological conditions	Stability class	D5
		F2
	Air temperature	293.15 K
	Humidity	50%

6. Results and Discussion

The study of anhydrous ammonia release, which has been carried out by Effects, has determined a mass flow rate equal to 0.36 kg/s and the released mass is 215 kg (Fig. 4). In order to reduce uncertainty of simulation, referred to ammonia cloud dispersion, it has been chosen the polytropic expansion model, because it is the most verisimilar condition in the real practice. Indeed polytropic expansion represents an intermediate transformation between purely adiabatic and purely isothermal. Extents of risk areas depend on atmospheric stability class. In fact passage from D5 to F2 produces an increase of extents of hazardous regions. In fact a higher wind velocity causes a stronger air flow and therefore an ammonia dilution improvement, which determines a noticeable decrease of the extents (Table 2). Ammonia concentrations have been calculated at the height of 1.7 m in order to take into account the human presence. Referring to stability class D5, the most hazardous thresholds LC_{50} and IDLH can be found as far as 39 m and 168 m from emission point (transfer pump), whereas, in case of stability class F2, the previous concentrations can be found as far as 96 m and 842 m. It follows that accident consequences could affect areas outside the industrial plant (Fig. 5). Risk areas are shown in Fig. 5, where a blue small cross indicates the release point. In such figure, "damage zones" boundaries are drawn in blue (stability class D5) and in orange (stability class F2), whereas "maximum exposure zones" boundaries are drawn in green (stability class D5) and in yellow (stability class F2).

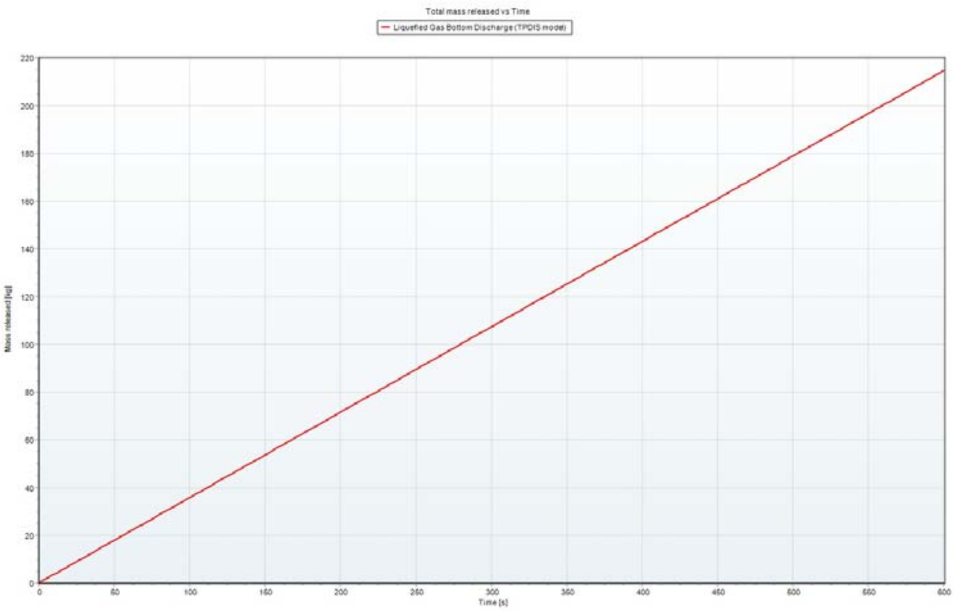

Fig. 4 Released mass (anhydrous ammonia).

Table 2 Results: extents of risk zones.

Accident scenario	Released mass (kg)	Atmospheric stability class	Maximum exposure distance (m) (LC_{50})	Damage distance (m) (IDLH)	Caution distance (m) (IDLH/10)
release from transfer pump	215	D5	39	168	612
		F2	96	842	2,824

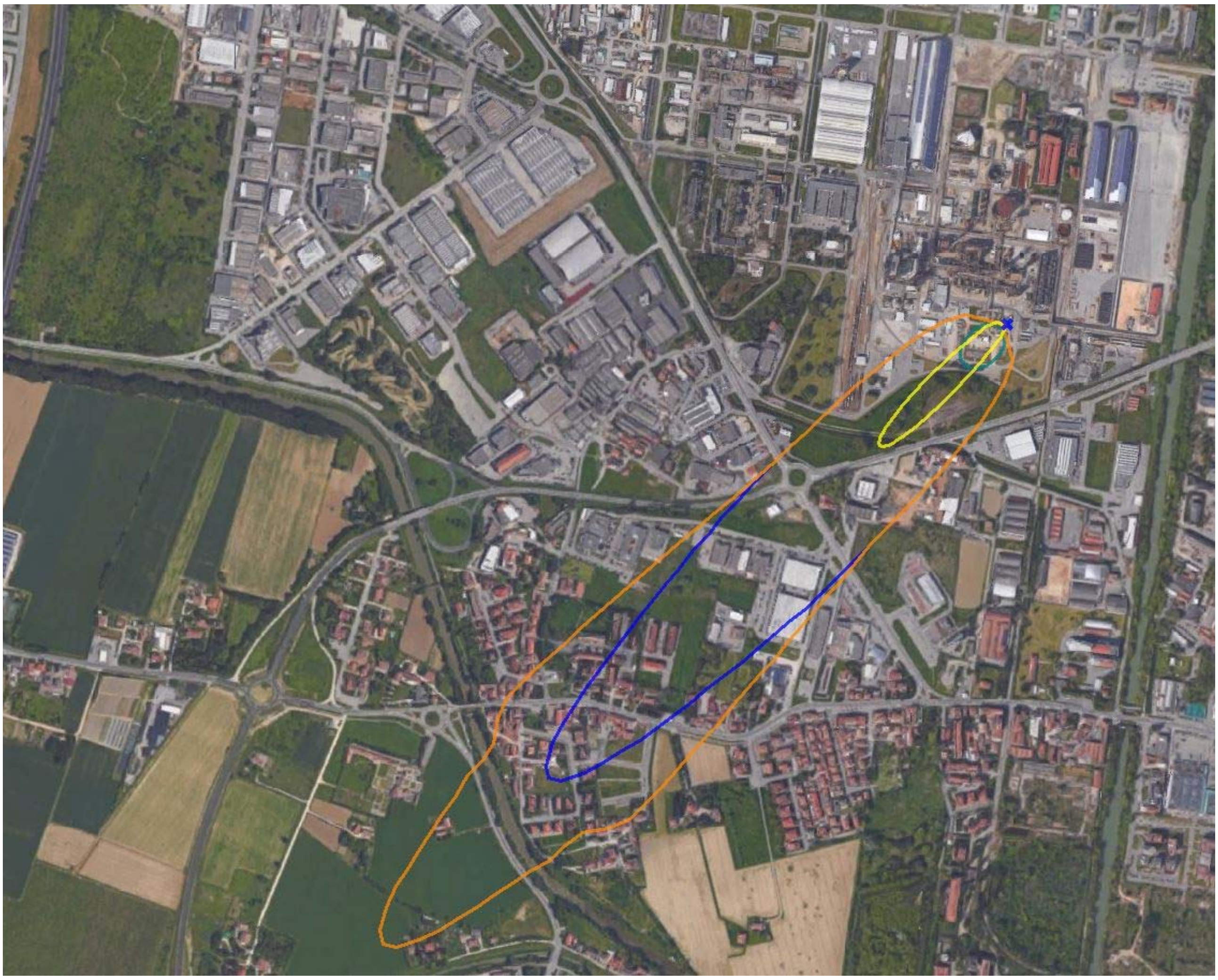

Fig. 5 Toxic release: risk zones.

7. Conclusions

Consequences assessment of anhydrous ammonia release has been carried out, basing on risk areas, depending on thresholds, which are dangerous to human health in Seveso plants. In order to reduce the unavoidable uncertainty of ammonia dispersion simulation, a careful study of its chemical and physical properties and plant operating conditions has been carried out. In addition to such analysis, statistical distribution of wind direction has been held in due consideration. This preliminary phase has allowed to select the most suitable model for studying toxic cloud dispersion. With regard to this aspect, the choice of expansion type assumes a very important role in case of emissions of toxic liquefied gases, because in these cases the two-phase release and the large quantity of aerosol in the cloud strongly influence gas dispersion (gases, that usually are lighter than air, act as heavy gases). In order to improve results accuracy, CFD models can be used and adapted to a wide variety of physical conditions, but there is an inherent uncertainty in the numerical predictions due to stability, convergence and accuracy. The importance of a well-placed mesh is highlighted in the modelling of two-phase flows in horizontal pipelines. The illustrated study has provided useful data, which have enriched information, required for improving external and internal emergency plan and verifying territorial plant compatibility.

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