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# A Risk Based Approach on Selection of Refrigerated Ammonia Storage

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Recently first edition of API STD 625 has been issued providing general requirements on refrigerated liquefied gas storage selection; according to this standard the selection of storage concept among the three alternatives (single containment plus dike, double containment, full containment, external or internal pumps) shall be supported by a risk-based approach analysis. The application of API STD 625 to refrigerated storage of ammonia is challenging since not practical configuration may be required to control the potential hazardous scenarios of ammonia, due to the large area affected by a huge release of liquefied ammonia in comparison with the one associated to similar release of a liquefied flammable gas. In fact the ammonia has a very low concentration limit leading to irreversible acute toxicity effect to humans. One of the main issues identified is associated to the current practice to have external pumps on refrigerated ammonia storage with respect to other applications (e.g. ethylene, liquefied natural gas) for which internal pumps are a consolidated design. A case study is presented: selection of 50,000 t Ammonia Storage inside an Ammonia Plant. The topics discussed highlight how further enhancement is required in order to make the safety performance of these facilities comparable with the ones of refrigerated liquefied flammable storage and how API STANDARD 625 provides a valid approach to identify critical issues to be discussed and improved.

## 1. Introduction

In the last 10 years there was a number of major accidents in industrial facilities that were caused by natural events. In some cases these events unfolded in such a way that their combination and intensity exceeded in negative way the operational scenarios considered in the design. As recent examples: earthquake that hit Japan in 2011 leading to partial core fusion in Fukushima Nuclear Plant and huge fire in Chiba refinery; Katrina Hurricane in 2005 causing serious damage to coastal industrial installation (Maxwell Shaffer, 2007).

Consequently a risk based approach is more often required to justify and support decisions on process selection and design configuration. In line with this approach, a new standard has been issued recently, Tank Systems for Refrigerated Liquefied Gas Storage (API STANDARD 625), providing general requirements on responsibilities, selection of storage concept, performance criteria, accessories/appurtenances, quality assurance, insulation and commissioning and in particular requiring a risk-based approach in selecting the storage concept. The adoption of Risk Based Approach (RBA) in support to the storage facility selection represents a key step of the design as it allows to take into account the risk posed by the hazardous scenarios associated to the facility which are identified and evaluated considering specific aspects such as geographic position, risk awareness, etc.

In particular API STANDARD 625 requires to perform the risk assessment in evaluating three alternative storage typologies, single containment plus dike, double containment, full containment. In addition for double and full containment type, the standard states that shell or bottom penetrations that breach the primary and secondary container are not allowed, i.e. internal pumps shall be provided, unless a number of additional requirements are met such as: in-tank valves are provided, the penetrations are accounted for in the assessment of risk etc.

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## 2. Application of API STANDARD 625 to Ammonia Storage

Ammonia is a toxic gas. It is mainly used as a source of Nitrogen in fertilizers, explosives and chemicals production plants. Ammonia is usually stored as liquefied gas and depending on the required capacity the following techniques are adopted (European Commission, 2007):

- Large scale storage: fully refrigerated storage at -33°C and in large atmospheric tanks with a typical capacity of 10,000 to 30,000 t (up to 50,000 t)
- Pressurized storage spheres or cylinders up to approximately 3,000 t
- Partially refrigerated tanks for intermediate capacities

For liquefied Ammonia Storage, the application of API STANDARD 625 may be challenging due to the combination of the following factors:

- Application of internal pumps suitable for liquefied ammonia is not consolidated, in particular when associated to large capacities. The design difficulties for this type of pumps are related to the need to avoid the contact of ammonia with copper members of the motor, currently this problem is managed using a magnetic coupling of motor and pump shaft (Rush and Kimmel, 2009), but this arrangement limits the maximum capacity of the pump. State-of-the-art is to have external pumps, while for flammable liquefied gas such as ethylene or liquefied natural gas, full containment tanks and internal pumps represent a consolidated arrangement.
- Application of in-tank valve is not consolidated and it implies accessibility and maintainability issues.
- The hazard area created by a huge release of liquefied ammonia is far larger than the one created by a similar release of a liquefied flammable gas since very low concentration of ammonia can lead to irreversible acute toxicity effect to humans, also considering prolonged exposure time associated to the duration of large pool evaporation. To support this consideration in Table 1 an example of comparison between hazardous scenarios from Ethylene Storage and Ammonia Storage with similar capacity is provided.

*Table 1: Example on hazardous scenarios in refrigerated tanks*

| Facility | Product | Hazardous Event | Hazardous Scenario | Threshold limit Value | Effect distance downwind from release point** |
|---|---|---|---|---|---|
| Refrigerated ethylene tank | Ethylene inventory 30,000 t | Catastrophic rupture | Flammable Cloud | ½ LFL* | 2,500 m |
| Refrigerated ammonia tank | Ammonia inventory 25,000 t | Catastrophic rupture | Toxic Cloud | 1 % Lethality | 9,000 m |
| Refrigerated ethylene pump discharge line | Ethylene pump flowrate 200 t/h | Pipe rupture (duration 15 min) | Flammable Cloud | ½ LFL* | 350 m |
| Refrigerated ammonia pump discharge line | Ammonia pump flowrate 200 t/h | Pipe rupture (duration 15 min) | Toxic Cloud | 1 % Lethality | 650 m |

*LFL Lower Flammable Limit

** calculations performed with Det Norske Veritas (DNV) Phast software assuming Pasquill atmospheric stability class F and wind velocity 2 m/s.

## 3. Case study: selection of Ammonia Storage within an Ammonia Plant

The case study selected is an Ammonia Storage located within an Ammonia Plant inside an industrial area. In the surroundings of the plant area various vulnerable receptors are present. In particular an airport at approximately 5 km NW and four major residential areas all around the plant at a distance in the range 6 to 10 km. Three alternative storage systems are considered:

- Single containment tank with external dike sized for 110 % storage capacity;
- Double containment tank (this option is usually not adopted for ammonia storage but it is kept as reference for comparison purposes);
- Full containment tank.

The risk analysis identifies the hazardous scenarios applicable to each storage typology, evaluated the consequences and mitigating measures and discussed the safety, design and feasibility/economic aspects concurring to the decision on the selection of the storage tank typology.

### 3.1 Design data

The Ammonia Storage under analysis is designed to receive ammonia from Ammonia Plant during normal operation and to receive ammonia from ships during first project stage when Ammonia Plant is not operating. Ammonia is stored as refrigerated liquefied gas at atmospheric pressure and at -33 °C.

Two ammonia tanks with 25,500 t of refrigerated liquefied ammonia each are provided. Tanks operating conditions are -33 ÷ -32 °C and 3 ÷ 8 kPa.

Ammonia from storage is partly pumped to users at 35 $m^3/h$ rate and partly sent to shipping via a pipeline when the Ammonia Plant is available and in operation. Shipping pumps rated capacity is 970 $m^3/h$, discharge pressure 750 kPa gauge, operating temperature -33 °C. In Figure 1 a simplified flow scheme depicts the Ammonia Storage arrangement.

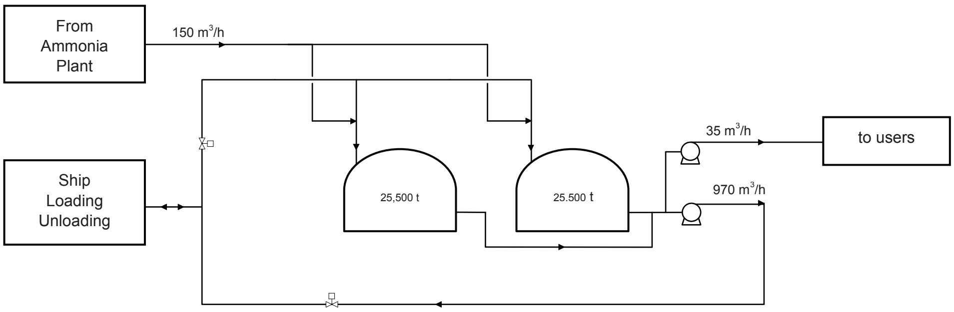

*Figure 1: Ammonia Storage arrangement simplified scheme.*

### 3.2 Identification of hazards associated with the refrigerated Ammonia Storage

From literature on ammonia facilities accidents (AIChE, 2012), one of the main contributors to loss of integrity in systems handling ammonia is Stress Corrosion Cracking (Blanchard, 2007). Stress Corrosion Cracking (SCC) is a degradation mechanism that is predominant in higher strength carbon steels. SCC is contingent on the presence of liquid ammonia and oxygen and is usually associated with welds where higher hardness occurs and residual stresses provide a source of tensile stresses. The susceptibility to SCC increases with increasing oxygen content. The risk of SCC is controlled and minimized by implementing proper design criteria, manufacturing and construction (welding) procedures, monitoring (Non Destructive Test) before start-up and proper start-up procedure and ensuring the presence of water in the stored ammonia (0.2% minimum). During tank life cycle Risk Based Inspection (RBI) is usually adopted to optimize inspection program. Nevertheless the possibility of a latent failure that might evolve in a rupture if associated to an additional load cannot be disregarded. API STANDARD 625 defines the design loads and the load combinations to be considered. The seismic loads are of particular interest. According to API STANDARD 625 and API Standard 620 refrigerated tanks shall be designed to ensure the safe containment of the stored inventory in case of a seismic ground motion having a 2% probability of exceedance within 50 years period, i.e. 2,475 years recurrence interval (Safe Shutdown Earthquake, SSE). However this scenario could be the additional load concurring to the rupture in case of a latent failure.

### 3.3 Selection of hazardous scenarios

On the basis of the considerations provided on possible causes of release, three representative release scenarios have been assessed. The frequency of occurrence is set as the frequency of occurrence of a Safe Shutdown Earthquake (SSE) adopting a reducing factor to take into account the concomitance of a latent failure (in the range 10 to 100).

Scenario 1. Rupture of single containment tank causing the release of the entire inventory inside tank dike. The pool extension is equal to dike area, and the scenario continues until the total vaporization of released ammonia. Frequency of occurrence range $10^{-5} \div 10^{-6}$ events/year.

Scenario 2. Rupture of primary liquid container in a double containment tank causing the release of the entire inventory inside secondary liquid container. The pool extension is equal to the annular space between primary and secondary shell (6 m wide) and the scenario continues until the total vaporization of released ammonia. Frequency of occurrence range $10^{-5} \div 10^{-6}$ events/year.

Scenario 3. Breach at penetrating nozzle in a full containment tank causing the release of liquid ammonia in open area. In case of provision of in-tank valve the release inventory is limited, while if the line cannot be isolated the scenario continues until the total vaporization of released ammonia. Frequency of occurrence range $10^{-5} \div 10^{-6}$ events/year.

### 3.4 Background risk from ammonia pumps and pipeline

In addition, as reference, two typical release scenarios representing the background risk associated to the ammonia pumps and pipeline have been assessed. The frequency of occurrence has been set, on the basis of International Association of Oil and Gas Producers (2010 a,b), at $7.5\times10^{-4}$ events/km/year for ammonia pipeline and $7.6 \times10^{-3}$ events/year for ammonia pumps.

Scenario 4. Release from shipping pump/pipeline. Leak from shipping pump seal (if external type) or pipeline leading to release of liquid ammonia in open area. The scenario duration depends on the operator intervention time to close emergency isolation valve on the line. For the scope of present study a time of 15 minutes is adopted.

### 3.5 Boundary conditions for hazardous scenarios evaluation

The scenarios have been evaluated with Det Norske Veritas (DNV) Phast release 6.7 using as main boundary conditions the following: Pasquill Weather Stability Class 2F and 5D, the first corresponding to stable atmospheric conditions, not favourable for dispersion; the second corresponding to less stable atmospheric conditions, more favourable for dispersion (Lees, 2001). Release Condition has been set as horizontal not impinging, at 1 m height. For unconfined releases, the ammonia pool surface is calculate by the software depending on release rate, evaporation rate, with the constrain of minimum pool thickness that has been set at 0.02 m.

### 3.6 Hazardous scenarios evaluation

Effect distances are reported as 1% Lethality and ERPG-3 at ground level. Lethality is calculated by means of DNV Phast probit function. ERPG-3 is defined in the Emergency Response Planning Guidelines (ERPGs), developed by the American Industrial Hygiene Association (AIHA), as the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to one hour without experiencing or developing life-threating health effects. For ammonia the most recent figure of ERPG-3 is set at 750 ppm (AIHA, 2011). The results of dispersion modeling are shown in Table 2, while in Figure 2 is provided an overlay of dispersion results in terms of 1% lethality on the GIS-map of the industrial installation and surrounding zones. It is anticipated that the software limits the release and the dispersion calculation to a maximum of 375 minutes. In case of prolonged releases such as scenarios 1, 2, and 3c, the results in terms of probit may be underestimated being the probit a function of concentration and exposure time.

*Table 2: Hazardous Scenario Dispersion Results*

| # | Scenario | Hole size | Duration | Leak rate (kg/s) | Max Pool radius (m) 2F / 5D | ERPG-3 distance (m) | | 1% lethality distance (m) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 2F | 5D | 2F | 5D |
| 1 | Collapse of single containment tank | - | >375 min | - | Dike 140mx140m | 50,000 | 14,500 | 9,400 | 2,500 |
| 2 | Release from 1st shell of double containment tank to 2nd containment | - | >375 min | - | equal to annular space between primary and secondary cont. | 6,700 | 2,200 | 3,300 | 1,500 |
| 3a | Release from penetrating nozzle (in-tank valve automatically operated) | 4”<br>10” | 1 min<br>1 min | 84.5<br>528.1 | 10 / 10<br>25 / 25 | 2,000<br>5,300 | 650<br>1,500 | 250<br>500 | 200<br>350 |
| 3b | Release from penetrating nozzle (in-tank valve remote operated) | 4”<br>10” | 15 min<br>15 min | 84.5<br>528.1 | 36 / 35<br>92 / 90 | 4,300<br>10,400 | 1,100<br>2,300 | 1,000<br>1,600 | 400<br>800 |
| 3c | Release from penetrating nozzle (without isolation) | 4”<br>10“ | >375 min<br>>375 min | 84.5<br>528.1 | 91 / 83<br>272 / 252 | 7,500<br>13,700 | 1,400<br>2,700 | 7,800<br>15,000 | 1,500<br>3,000 |
| 4 | Release from shipping pump or pipeline | 1”<br>4” | 15 min<br>15 min | 11.6<br>186.0 | 7 / 2<br>47 / 45 | 1,200<br>3,900 | 500<br>1,600 | 300<br>1,000 | 250<br>650 |

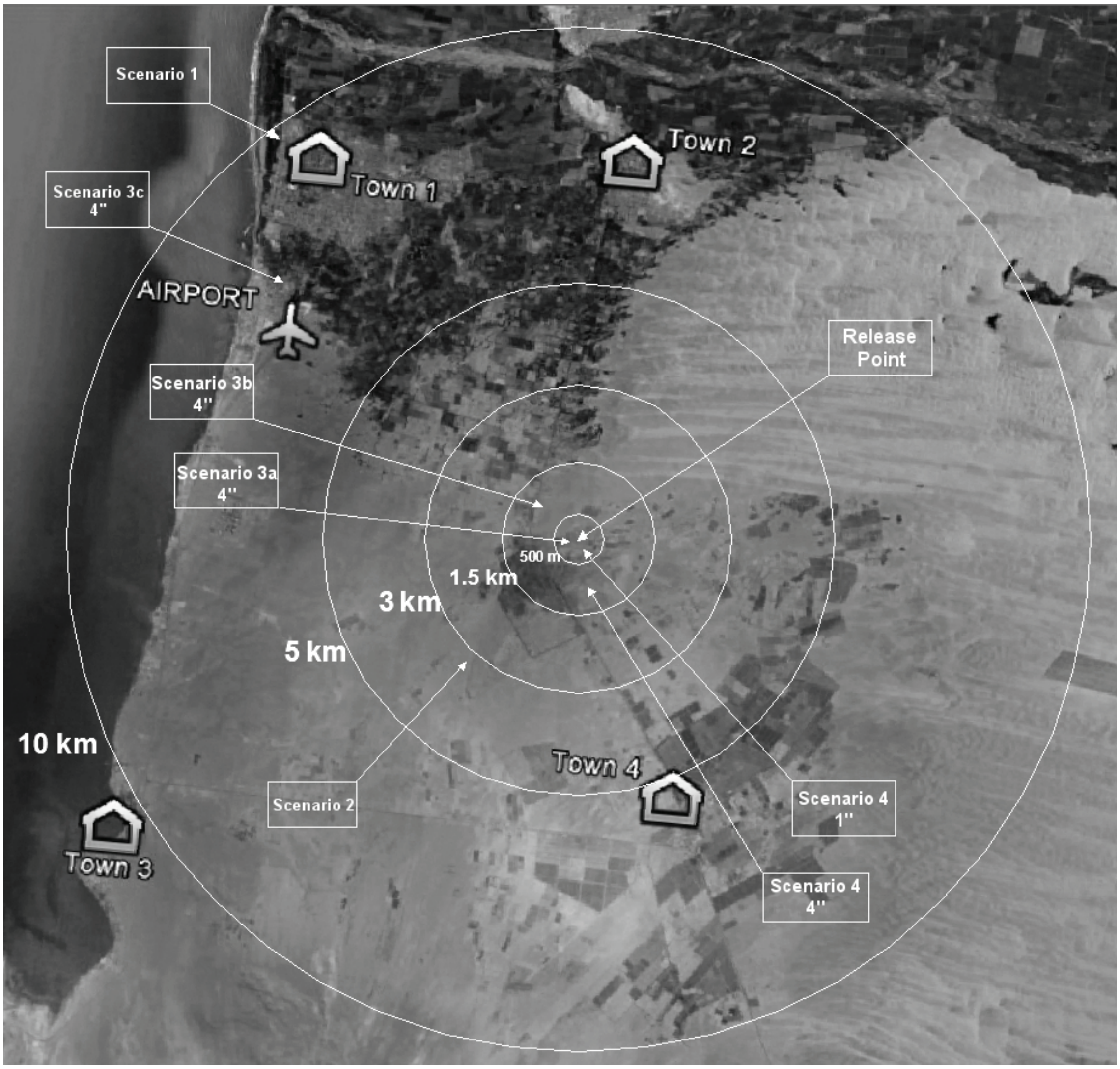

*Figure 2: 1% Lethality maximum extension (worst weather condition)*

### 3.7 Discussion on results

The background risk associated with handling of liquefied refrigerated ammonia at shipping capacity is represented by scenarios 4. The impacted area associated with 1% lethality is limited (maximum 1 km). An extensive area may be exposed to health effects in case of prolonged exposure (ERPG-3 up to 3.9 km distance from the release). The risk posed by the pipeline can be reduced within acceptability thresholds acting on pipeline routing, design condition, protective measures against external impact and internal corrosion, and leak detection system. The residual risk can be managed implementing External Emergency Response Plan.

The scenarios associated to the configuration of single containment tank plus dike (scenario 1) and double containment tank (scenario 2) lead to very large impacted areas potentially affecting populated locations. These storage typologies are not acceptable since no effective mitigating measures can be implemented to reduce the risk.

For the configuration of full containment tank with external pumps a significant risk scenario is present (scenario 3). The main concern for this configuration is the pump suction line penetrating both primary and secondary containment. In case of non-interruptible release, corresponding to release scenario number 3c, very large impacted areas potentially affecting populated locations would be created. Provision of in-tank valve, recommended in API STD 625, has been investigated. Release scenario number 3b, corresponding to in-tank valve activated remotely by operator (release duration 15 min), and scenario number 3a, corresponding to in-tank valve automatically activated (release duration 1 min), have been analysed. In both cases the impacted area associated with 1 % lethality is limited (maximum 1.6 km), and an extensive area may be exposed to health effects (ERPG-3 up to 10.4 km distance), requiring an extensive External Emergency Response Plan to be put in place.

Based on the risk assessment performed, full containment tank with internal pumps results in lower hazard distances (only back ground risk applies). However, as discussed, provision of internal pumps for the required shipping capacity is not currently feasible since no references are available for high capacity internal pumps in refrigerated ammonia storage. In addition the case study includes considerations on the future installation of a second stage Refrigerated Ammonia Tank with same capacity for which common external shipping pumps are preferable.

Alternate solutions have been investigated, such as provision of in-tank valves which is unusual for refrigerated ammonia tanks and implies in-tank accessibility and maintainability issues. Therefore, the selected option for this case study is a full containment tank with external pumps without in-tank valves. Mitigating measures adopted in order to minimize the risk of rupture of penetrating nozzle are to overdesign the secondary container penetrating nozzle, taking into account the dynamic stresses during an earthquake, ensuring that the weak point on the penetrating line is on the primary container nozzle. The nozzle protruding outside the secondary containment shall be integral forged piece with junction weld between the two containment shells. Additionally, external emergency isolation valve welded to tank nozzle bellow to isolate tank inventory in case of leak in the downstream pipe/pumps shall be provided.

## 4. Conclusions

The state-of-the-art design on refrigerated storages provides an acceptable level of risk with regard to storages applied to flammable product (liquefied natural gas, Ethylene, …), however the same design could not ensure a comparable acceptable level of risk for very highly toxic products like ammonia. The topics discussed and in particular the case study presented highlight how for the current huge capacities of refrigerated liquefied ammonia storage, further enhancement are required in order to make the safety performance of these facilities comparable with the ones of refrigerated liquefied hydrocarbon storage. For this scope API STANDARD 625 provides a valid approach to identify critical issues to be discussed and improved in a very early design phase when decisions on system arrangement, capacity and lay-out are to be made.

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