$DeNO_X$ PLANTS: SAFETY IN UNLOADING AND STORAGE OF AQUEOUS AMMONIA

Roberto Lauri
Inail - Settore Ricerca, Verifica e Certificazione Dipartimento Innovazioni Tecnologiche e Sicurezza degli Impianti Prodotti e Insediamenti Antropici (DIPIA)
Roma
r.lauri@inail.it

$DeNO_X$ plants, which are used to reduce NO_X emissions from power plants, can generate hazards. In fact one of the major hazards is the formation of a toxic and flammable vapor cloud from an accidental release of ammonia. In this contest the water spray curtain is currently recognized as a reliable technique to mitigate toxic and flammable vapors and increase safety standard of the aqueous ammonia tanks storage area

Impianti $DeNO_X$: sicurezza nello scarico e nello stoccaggio dell'ammoniaca acquosa
Gli impianti $DeNO_X$, utilizzati per ridurre le emissioni di NO_X delle centrali termoelettriche a vapore, possono generare situazioni pericolose, dovute alla formazione, in seguito ad accidentali rilasci, di vapori tossici ed infiammabili di NH_3. In questo contesto la cortina d'acqua viene correntemente riconosciuta come un'affidabile tecnica per mitigare le conseguenze di vapori tossici ed infiammabili ed incrementare lo standard di sicurezza dell'area di stoccaggio della soluzione ammoniacale.

Introduction

Selective Catalytic Reduction (SCR) of NO_X by ammonia (NH_3) is widely applied to reduce NO_X emissions from power plants. Nowadays hundreds of SCR systems ($DeNO_X$ plants) are successfully operating in Japan, Europe and United States. $DeNO_X$ plants can utilize either aqueous or anhydrous ammonia for the nitrogen oxides reduction. SCR applications, which use aqueous ammonia, generally store it at a concentration of 25% ammonia in water, though recent applications utilize a 19% solution. The OSHA (Occupational Safety and Health Administration of the USA) classifies anhydrous ammonia as a "highly hazardous" chemical substance. Aqueous ammonia, although less concentrated than anhydrous ammonia, poses similar risks and requires a bigger storage capacity. Ammonia solutions are corrosive to the skin and eyes, while vapor phase is harmful to mucous membranes and may create explosive mixtures. In fact one of the major hazards is the formation of a toxic and flammable ammonia vapor cloud from any accidental release. The paper describes some systems, that allow to increase safety in unloading and storage of aqueous ammonia. In particular a technique, which is commonly used for its dispersion and absorption abilities on a NH_3 cloud, is described. This technique is the "water curtain".

Aqueous ammonia: primary hazards

Aqueous ammonia reacts with human tissues in different degrees, which depend on the concentration and duration of the exposure. Ammonia vapors can be suffocating and irritating to mucous membranes (Tab. 1).

Tab. 1 - Ammonia exposure effects

Readily detectable odor	20-50 ppm
Severe irritation of nose, eyes and throat	400-700 ppm
Dangerous (less than ½ hour exposure may be fatal)	2,000-3,000 ppm
Serious edema, asphyxia, strangulation (rapidly fatal)	5,000-10,000 ppm
Immediately fatal	>10,000 ppm

There are significant risks, that are associated with its transport, unloading and storage. Since many trucks or railcars must be unloaded every day, the potential risks are elevated. Storage tanks present a bigger hazard, because $DeNO_X$ plants require ammonia storage volumes in the range of several hundreds of liters. In the event of a storage tank failure or leakages from pipelines and valves an ammonia cloud could form and be lethal.

Aqueous ammonia unloading

Ammonia solution delivery is made by cargo tank transports. Transfer of material from the cargo tank trucks to the storage tank is usually effected by pumps or compressors or a source of compressed air or nitrogen[1]. If compressed air or N_2 are used to effect the delivery, the pipings system includes a backflow check valve in order to prevent that ammonia vapors can enter the air or nitrogen line.

Aqueous ammonia unloading: "pump" method

The pump may be mounted on the cargo tank transport (Fig. 1) or it may be a part of the receiving storage system.

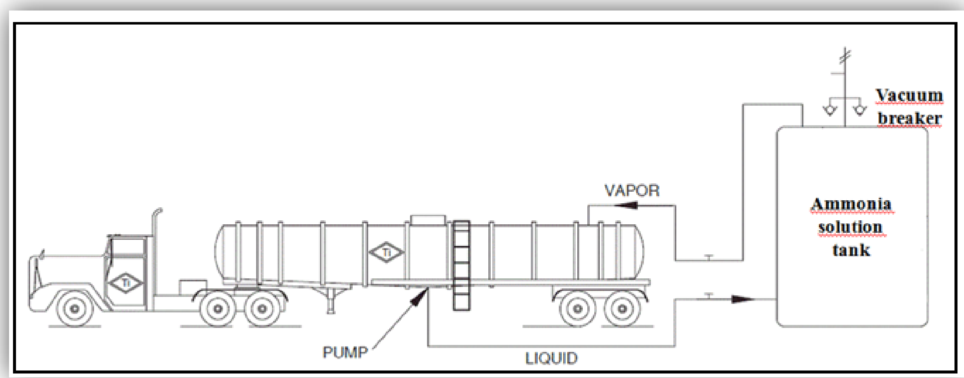

Fig. 1
Pump method

It should be kept in mind that the vapor pressure of the aqueous ammonia is about equal to atmospheric pressure and that any suction pressure could cause the ammonia vapor comes out of solution and so a vapor lock occurs. Systems should be designed so that the pump is near to the hose connection and that the hose length is as short as possible (about 6-7 meters).

Aqueous ammonia unloading: "compressor" method

Trucks can be equipped with compressors, which can produce about 1,5 barg differential pressure. Air or vapor pressure is used to push ammonia solution out of the cargo tank into the storage tank (Fig. 2).

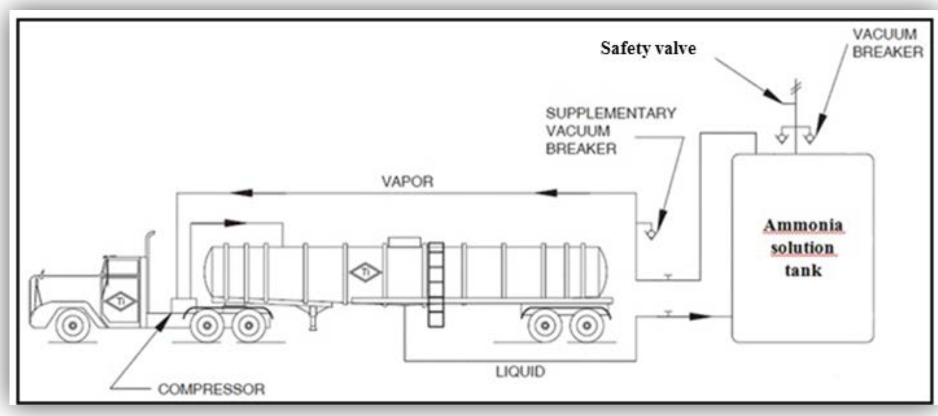

Fig. 2
Compressor method

Some provision must be taken to prevent the buildup of pressure in the storage tanks[2], which are rated for 2-3 barg. This event can be avoided if the compressor vapor can escape to a scrubber system. If a scrubber system is used, it can be constituted by a water container. The vapors are introduced into the water by a sparger, which produces small bubbles for easier absorption. If the vapor is fed by the compressor to the cargo tank, precautions should be taken to insure that the storage tank is not exposed to substantial vacuum. A vacuum on the storage tank could result in its collapse, that could cause hazardous consequences. The possibility of a vacuum in the storage tank is prevented by a supplementary vacuum breaker.

Ammonia solution properties

$DeNO_X$ plants, which use aqueous ammonia, generally store it at a concentration of 25% ammonia in water, though some recent applications utilize a 19% solution. Tab. 2 gives the properties of a 25% aqueous ammonia solution.

Tab. 2 - Ammonia solution properties

Properties	Aqueous ammonia
Concentration of reagent	25% (by weight of NH_3)
Molecular weight of reagent	17,03 (as NH_3)
Density (T=20 °C)	0,87 g/cm^3
Vapor pressure (T=20 °C)	23 hPa
Flammability limits in air (ammonia vapor)	16-25% NH_3 (by volume)
Short-term exposure	35 ppm
Odor	Pungent odor (≥5 ppm)
Acceptable materials for storage	Weldable structural steels in accordance with EN 10025, fine-grained steels in accordance with EN 10028-3, stabilized stainless austenitic steels and stainless austenitic steels with a carbon content ≤0,03% in accordance with EN 10028-7 (storage pressure is about 2 barg)

Aqueous ammonia storage system

The storage tanks are above ground, cylindrical and normally horizontal and surrounded by a catch basin[3]. The truck unloading pad is equipped with a catch basin and a drain line, which diverts any leakage from a truck into a large sump located within the basin. All connection pipings and the supply pumps are usually located inside a different basin, while controls can be located outside. Emergency showers are located both inside and outside the basin. Ammonia detectors are located within the storage area for both local and remote alarm to the control room. Two 100% capacity supply pumps in the tank area maintain a constant recirculation feed loop through the storage tanks. This loop supplies a flow to a single supply line, which feeds a common plant header. The single supply line is equipped with its own electronic leakages detection system. Flow to each unit is independently controlled from this common header. In an emergency situation, the ammonia supply system can be remotely shut down from the control room. Otherwise all controls are local to the storage tanks area.

Safety aspects for aqueous ammonia tanks

The following considerations must be made to ensure safety of storage tanks and connected operations:
1) dual measurements for tanks level and pressure;
2) remote shut-off valves on aqueous ammonia inlet and outlet line from storage tank[4];
3) ammonia leakages detection system (both aqueous ammonia and ammonia vapors) for the storage installation;
4) adequate fire water grid and water curtains around ammonia pumps, storage tanks and tankers unloading stations;
5) lightning conductor;
6) emergency lighting;
7) safety and vacuum relief valves;
8) redundancy in critical instrumentation and control[5];
9) catch basin to collect the possible leakages of aqueous ammonia.

Instrumentation and control systems must allow normal operation of the tanks, without requiring personnel to enter the storage area. All controls must be accessible outside the basins and all indicators must be visible.

Tank pressure: safety devices

The devices, that indicate and relieve the pressure, must be in accordance with EN 764-7. The storage vessel must be equipped with a continuously and operating remote pressure indicator. The alarm signal, which is released in the case of pressure excess (overpressure), must be transferred to a permanently manned location (control room). The storage tank is equipped with two safety valves[6] and only one of which must be permanently ready for the operation. A change-over system ensures that the required discharge area is maintained at all times. In this case it is assumed that aqueous ammonia is never present at the safety valve. The storage vessel is provided with a vent valve to prevent vacuum conditions. Vent and discharge pipes of the storage tanks are provided with flame arrestors in order to decrease the effects of possible explosions (ammonia vapors are flammable).

Measuring and limitation of the aqueous ammonia level

The aqueous ammonia tank can be filled to 85% of its total volume to allow a vapor space above the liquid level. The ammonia solution level in the vessel is maintained by the level controller, that adjusts the liquid flow[7]. For each storage vessel two independent and protective devices against overfilling (filling level limiters) are required and the suitability of the level indicator must be proved. The indication of the liquid level is transferred to the control room. One of these devices may be integrated into the liquid level indicator. The two protective devices against overfilling operate by different principles in order to ensure a continuous operation of the protection system. The control pulses actuate the safety shut-off devices of the filling system on the vessels and of the filling installation as well as the feed pumps. If one of the protective devices against overfilling responds, the safety shut-off valves and the pumps must interrupt the supply flow, and at the same time, an alarm signal sounds at the filling location.

Ammonia cloud mitigation

Aqueous ammonia releases create a pool in the catch basin. Ammonia can evaporate from the liquid pool and generate a toxic and flammable cloud. There are various techniques to reduce NH_3 concentration in the cloud under toxicity and flammability levels in order to decrease the hazardous area. A mitigation technique[8], which is commonly used in the $DeNO_X$ plants, is the water curtain, because ammonia gas is highly soluble in water (its solubility in water is 517 g/l at 20 °C). This is one of the most economic and efficient techniques of ammonia vapors mitigation.

Water curtains

The water curtain uses an induced air flow to enhance the dilution of the cloud. This technique consists of a rack, that is equipped with a uniform distribution of nozzles (Fig. 3). As the spray induces an air entrainment, the ammonia cloud is diluted.

This entrainment takes place as the result of the transfer of momentum from the water drops to the ambient air[9] and depends on many factors such as spray configuration, drops size, velocity distributions and the nozzles spacing.

The action of a water curtain is threefold: the mechanical dispersion by air entrainment, the mass transfer by chemical absorption and the heat transfer due to temperature differences.

Fig. 3
Downward water curtain

This mitigation technique mainly enhances NH_3 vapors cloud dispersion by two mechanisms:
1) forced dispersion and dilution;
2) absorption.

The ammonia concentration (C_{NH3}) in the cloud (with curtain) is given (kg/m^3) by:

$$C_{NH3} = m_{NH3}(1-r)/(Q_a+Q_{awc}+Q_{NH3})(1-r) \qquad 1)$$

where:
- m_{NH3} is the ammonia mass flow rate (kg/s);
- Q_a is the air volumetric flow rate (m^3/s);
- Q_{awc} indicates the volumetric air flow (m^3/s), which is induced by the water curtain (vapors dilution);
- Q_{NH3} is the ammonia volumetric flow rate (m^3/s);
- r is the absorption factor (adimensional parameter).

In absence of water curtain Q_{awc} and r are zero. The removal potential of water curtains to mitigate unconfined releases of water soluble gases (ammonia), has been investigated in many large-scale experiments. Results, which are reported in literature, show that the water barrier can absorb up to 80% of the released ammonia when the ratio between the mass flow of the injected water and the mass flow of the ammonia vapors is over 70[10]. Releases and vaporization rates under the worst conditions must be used to determine the maximum water flow. The water also has a cooling effect, which is an important factor in order to prevent cloud explosion. The water curtain is a fixed and perimetric barrier, which surrounds the entire catch basin, including the storage tanks. The nozzles may be automatically switched on in case of an accidental release. The first step to minimize the consequences of an ammonia release is a prompt detection of the leakage. Ammonia vapors detectors are installed in critical locations around the aqueous ammonia storage area in order to transfer an alarm signal to the control room. This alarm determines the water curtain activation. The detectors number is redundant in order to ensure the detection continuity. In case of a gas dispersion on an industrial site, an early detection and the wind direction are essential informations. The water curtains usually generate a vertical spray, in downward or upward operating mode. For the mechanical effect (dispersion) upward water curtains have generally been recognized most efficient than the downward curtains. Nozzles spacing influences curtain efficiency. In fact if the distance between the nozzles is large, the ammonia cloud may bypass the water curtain through empty spaces. There are mainly three types of nozzles, which produce different flow patterns:
- the full cone nozzle develops in a circular cone. The spray angle may vary from 30° to 130°. A large nozzle orifice results in a large flow number and a coarse droplet spray. A model of the full cone nozzle is shown in Fig. 4. Some nozzles are equipped with a swirl chamber such that the liquid is put into rotation. The full cone spray is more effective in creating turbulence closer to the spray region than the flat fan spray;
- a hollow cone nozzle has a similar envelope of that of the full cone nozzle, however, the inner part of the spray is free of droplets;
- the flat fan nozzle produces a flat elliptic cone (rectangular or trapezoidal distributions of liquid are also possible). High-energy jets are generated with spray angles up to 60 °C. This nozzle is more effective in reducing the ground level concentration by creating a barrier in the path of the cloud and pushing the cloud upward.

Their aim is to produce very small droplets, which are essential for absorption effects.

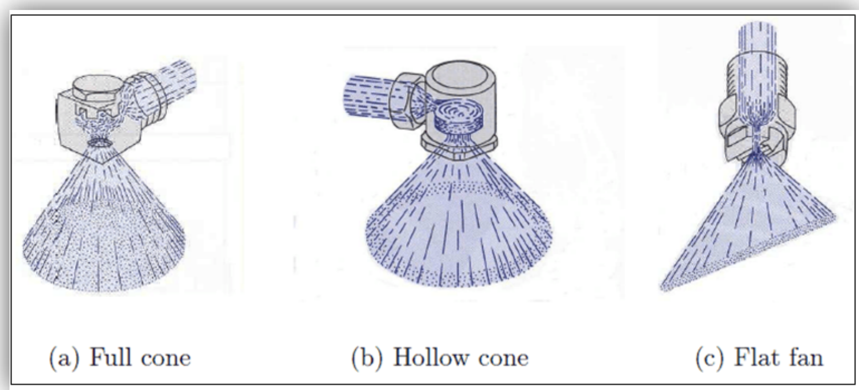

Fig. 4
Different types of nozzles

Ammonia absorption

An action of the water curtain is the absorption of the vapors by water droplets. It depends on the gas solubility in water and may be negligible under certain conditions.

For example, for low soluble gases as liquefied natural gas absorption is very poor.
Additives in the water can accelerate or create a chemical reaction for low soluble gases. However, it can be an efficient mean to enhance the vapors mitigation for highly soluble gases (ammonia). In opposition to mechanical dispersion, absorption causes an ammonia removal from the cloud. In this way, the mitigation is not only around the water curtain but also faraway. The droplet diameter is the critical parameter for absorption. A smaller droplet absorbs faster because the interfacial area is more important and the contact time is longer.

Water curtain effectiveness

The effectiveness of a water curtain depends on various parameters, which can be divided into two groups:

- parameters of its own characteristics: water droplets distribution, nozzles type and size, width, length, water pressure, etc.;
- external parameters: ammonia properties, wind speed, atmospheric stability, etc.

The effectiveness is given by the ratio between the air volumetric flow rate (this flow is induced by the water barrier) and the injected water volumetric flow rate. There are various empirical equations for the effectiveness estimation. The Watcur Model[11], which considers both dilution and absorption, uses the following equation:

$$\ln Y = A + A_1/M_1 + A_2/\ln M_1 \qquad 2)$$

where:

- Y indicates the effectiveness;
- A, A_1 and A_2 are experimental coefficients. A ranges between 2 and 2,8. A_1 is approximately -0,6 and A_2 is -0,05. These values are referred to flat fan nozzles, which have a spray angle of 30° and are located at 3 meters one another;
- M_1 indicates the water volumetric flow rate per curtain length (l/s/m).

Conclusions

Ammonia solution unloading and storage can trigger dangerous situations in the $DeNO_X$ plants. Safety measures, that prevent and control accidental releases and reduce their consequences, are essential. In this context the water curtain is a reliable technique to protect the employees and the public from injury or harm. This safety measure is especially important for aqueous ammonia storage tanks, which are installed in $DeNO_X$ plants, because it has a dual function of mitigation: absorb a water-soluble vapor cloud (NH_3 is highly soluble in water) and dilute a flammable vapor cloud. On the contrary water curtain mainly enhances LNG (liquefied natural gas) vapors cloud dispersion by mechanical effects (forced dispersion and dilution), because the solubility of the LNG in water is minimal (absorption can be ignored). The advantages of the water curtains are the readily available water, the low operating cost and the simple operation. The disadvantage of downward water curtains is the limited access for maintenance and for upward curtains the disadvantages are the possible damages, because they are placed at ground level.

REFERENCES

[1]Energy Institute, Environmental risk assessment of bulk liquid storage facilities: A screening tool, 2009.
[2]J. Chang, L. Cheng-Chung, *Journal of Loss Prevention in the Process Industries*, 2006, **19**(1), 51.
[3]D.P. Tonn, A. Kokkinos, D. Monnin, SCR system operating experience at AES Somerset, Power-Gen International 2002**,** Orlando, 10-12/12/ 2002.
[4]G.S. Lele, *Chemical Industry Digest*, May 2008, 85.
[5]J. Yuill, A discussion on losses in process industries and lessons learned, 51st Canadian Chemical Engineering Conference, 2001.
[6]European standards EN 12952-14 **"**Requirements for flue gas $DeNO_X$ systems using liquefied pressurized ammonia and ammonia water solution", March 2005.
[7]Center for Chemical Process Safety, Guidelines for risk based process safety, 2007.
[8]J.M. Buchlin, Water sprays as mitigation means, International Workshop on Multiphase and Complex Flow Simulation for Industry, October, 2003.
[9]J. McQuaid, R.D. Fitzpatrick*, Journal of Occupational Accidents,* 1983, **5**(2), 121.
[10]A. Dandrieux *et al.*, *Journal of Loss Prevention in the Process Industries,* 2001, **14**(5), 349.
[11]G. Drogaris, WATCUR Programme for estimating water curtain efficiency in mitigating heavy gas releases, Technical Note I.92.31, April, 1992.