Explosion of an aqueous ammonia scrubber tank at Yara Italia, Ferrara

The formation of explosive gas mixtures in atmospheric aqueous ammonia solution tanks is sometimes an underestimated risk as ammonia/air gas mixtures are generally very difficult to ignite. However hydrogen entrainment and accumulation can significantly impact on the explosion risk level as the example of the explosion incident at Yara Italia, Ferrara illustrates.

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Introduction

This paper describes the findings and recommendations from a detailed technical investigation of the explosion incident of an aqueous ammonia scrubber tank in October 2009 at Yara Italia, Ferrara plant.

Description of process

The vapors returning from the aqueous ammonia storage tank, D1301, and from the truck loading stations 1+2 are passed through a scrubber column before being discharged into the atmosphere. The scrubber, C 1301, has two sections as shown in Figure 1. Fresh demineralised water is added to the upper section to perform the final scrubbing. A weak ammonia solution is recycle used to the lower section to remove the bulk of the ammonia from the D1301 vapor stream.

The scrubber liquor is collected in a tank below the scrubber as a weak ammonia solution at a typical temperature of 25-35 °C.

The scrubber liquor is used as make-up water for the aqueous ammonia production. It is mixed with heated ammonia from the cold storage in the ammonia/water in-line mixer and sent to D1301. When no aqueous ammonia is produced the surplus scrubber liquor is sent to the urea plant for ammonia recovery.

The concentration of the scrubber liquor is not measured. However the inflow of fresh water at the top of the scrubber ensures a constant dilution of the weak ammonia solution in the scrubber tank (typically <2 wt-% NH3). The flow rate of fresh water is manually set as per operating instruction.
Figure 1: Flowsheet of the aqueous ammonia production unit

An additional aqueous ammonia stream is occasionally sent to the ammonia scrubber tank from the ammonia plant purge gas scrubber, C3502. C3502 removes the ammonia from the synthesis loop purge prior to the membrane hydrogen recovery unit. This purge gas scrubber operates at high pressure (120 to 140 bar) and the aqueous ammonia solution contains some physically dissolved hydrogen which is released in C1301.

The scrubbing unit C1301 was installed in 2009 based on inhouse design by Yara Project Office as a replacement of an older installation.

Description of incident and sequence of events

During a thunderstorm on 12 October 2009 at 12:07h an incident occurred in the aqueous ammonia production facility at Ferrara that resulted in severe damage to the aqueous ammonia scrubber tank.

The incident led to a complete deformation of the tank bottom and reinforced tank top, ripped the anchor bolts out of the concrete foundation and cracked open the bottom weld over approximately 90% of its circumference. The tank and the directly connected scrubber column were lifted-up (2 to 3 m) due to the jet release of the scrubber liquor from the failed bottom weld. The lifted tank displaced and toppled the steel support structure coming to rest at some 5m distance.

As there were no people in the vicinity at the time of the incident no personnel were injured. Also the released scrubber liquor was contained inside the bunded area and eventually fully recovered in a spillage tank.

Scrubber tank and connected piping incl. instrumentation and valves were severely damaged (some beyond repair).

Sequence of events

<p>| 11 Oct | 00:00h | Preparation of aqueous ammonia solution; Aqueous ammonia bleed from purge gas recovery units is send to C1301 at a flow rate of 2.5 m3/h |
| 06:14h | Stop of aqueous ammonia preparation |
| 06:15h | Stop sending aqueous ammonia bleed from the purge gas units to C1301 |
| 12 Oct | 11:00h | Start loading 1st truck (25% NH3-sol.) |
| 11:40h | Stop loading 1st truck – total load 29.9t |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:07h</td>
<td>Accident occurs and all DCS-signals switch to IOP or malfunctioning; Shift supervisor orders field operator to do a field check of the aqueous ammonia production unit</td>
</tr>
<tr>
<td>12:10h</td>
<td>Shift supervisor arrives at the scene of the incident and initiates the emergency response activities in accordance with the applicable emergency procedures</td>
</tr>
<tr>
<td>12:13h</td>
<td>Loading of the 2nd truck is interrupted – total load 15.6t</td>
</tr>
<tr>
<td>12:30h</td>
<td>The two trucks on loading during the incident are stopped at the gate for an gas-phase-analysis (1st truck: 83 ppm hydrogen; 2nd truck: 62 ppm hydrogen); Both trucks are cleared for dispatch; The concentration of the recovered solution is regularly monitored (lab results: 12:40h: 340 ppm ammonia; 13.40: 5 ppm ammonia)</td>
</tr>
</tbody>
</table>

**Extent of damage**

The C1301 scrubber tank was heavily damaged as seen in Figures 2, 3 and 4. Further damage was caused to the surrounding equipments and piping by the lifting/displacement of the tank.

By contrast, the scrubber column connected centrally on top of the aqueous ammonia scrubber tank remained basically intact except for minor damages as shown in Figure 5.
These damages occurred mainly when the tank and scrubber hit the side wall of the neighboring building and fell back down to the ground.

The main piping connected to the scrubber and tank were destroyed and could not be re-used.

The steel support structure for the scrubber column which was partly placed above the tank got tilted to the side partially deforming but was repairable as shown in Figure 6.

![Figure 6: Tilted support structure to access scrubber](image)

The collateral damage to other buildings and installations in the area was minor.

The total costs for repairs/reconstruction and technical improvements were in the range of 400 kEUR (respectively 520 kUSD).

**Root cause of the incident**

Based on the damage suffered it was apparent that the aqueous ammonia scrubber tank C1301 was exposed to an instantaneous, excessive overpressure. This overpressure has been identified as the direct cause of the incident.

The pressure increase was only recorded in the DCS-system as a pressure peak of the pressure indicator located in the vapor return line from the truck loading stations. However, the maximum pressure was not recorded as the pressure increase was too fast for the normal DCS-measuring frequency. There was also no indication from the pressure gauge placed on top of the scrubber. Hence, the maximum overpressure leading to tank rupture needed to be determined theoretically using methods of fracture mechanics.

**Determination of maximum overpressure prior to tank rupture**

Based on the documented extent of the damage the following failure mechanism was assumed:

The scrubber tank was fixed to the foundation with anchor bolts (which were fixed in the concrete foundation with epoxy glue) to prevent horizontal movement of the (empty) tank due to wind forces.

Once the internal overpressure induced sufficient high forces to rip out these anchor bolts the bottom plate bulged. This caused a high bending moment in the area of the circumferential bottom weld which superposed with the pressure induced (axial+tangential) stresses in the plate material.

As a consequence the max. tolerable yield stress of the plate material in the heat affected zone was exceeded and the tank bottom cracked open.

A finite-element-model was developed to provide a qualified estimate of the maximum internal overpressure. For simplification purposes it was assumed in the calculation that all anchor bolts got cracked though they were actually ripped out of the concrete without any visible damage to the anchor bolts themselves.

Based on this assumption the calculation showed that the tank could withstand an internal overpressure up to 0.7 to 0.9 bar(g).

Without any anchor bolts in place (or all loose) the maximum overpressure would have only been in the range of 0.1 bar(g).

**Evaluation of possible incident scenarios leading to overpressure**

In principle three incident scenarios were identified that could potentially have caused excessive
overpressure inside the aqueous ammonia scrubber tank:

1. Flash evaporation of the aqueous ammonia solution inside C1301
2. Backpressure from the aqueous ammonia loading facilities combined with a blockage of the vapour outlet from the scrubber
3. Explosion inside the aqueous ammonia scrubber tank due to ignition of an explosive ammonia/air gas mixture
   - explosive ammonia/air gas mixture
   - explosive hydrogen/air gas mixture.

All three incident scenarios were taken into consideration in the root cause analysis and evaluated to the extent necessary.

From the systematic root cause analysis the following general conclusions were drawn:
- Scrubber, aqueous ammonia scrubber tank and aqueous ammonia loading facilities were operated according to operating procedure.
- Available DCS-data and interviews with the operating staff did not reveal any operation errors or loop-holes in the operating procedure.

As a consequence the following was assumed with very high likelihood:
- No instantaneous or slow backpressure built up in the aqueous ammonia scrubber tank ruling out incident scenario 2.
- No strong liquid ammonia solution flow (or pure liquid ammonia flow) entered into the aqueous ammonia scrubber tank as there was no temperature rise measured inside C1301 prior to the incident. Thus incident scenario 1 was ruled out.

These conclusions leaves the ignition of an explosive gas mixture inside the aqueous ammonia scrubber tank as the most likely incident scenario. The further investigation mainly concentrated on verifying the presence of an ignition source and finding a plausible root cause for the formation of an explosive gas mixture.

Formation of explosive ammonia/water/air mixtures

In principle scrubber tank C1301 is designed as a non pressurised vessel, open to atmosphere via the vent line of the scrubber column. Consequently the presence of air in the gas phase above the scrubber liquor is inevitable as no nitrogen blanketing was installed.

In an atmospheric tank without blanketing the formation of an explosive ammonia/water/air mixture is principally possible once the strength of the scrubber liquor reaches a minimum ammonia concentration so that the related ammonia vapour pressure exceeds the lower explosion limit for ammonia/water/air mixtures (which is at about 15 vol-% ammonia in air).
This minimum ammonia concentration can be as low as 5 to 10 wt-% if the scrubber liquor temperature is in the range of 40 to 50 °C.

Review of process design

The process design review performed during the engineering phase for the new installation did not explicitly consider the possible formation of an explosive gas mixture. This assumption was re-evaluated as part of the technical investigation.

Following a detailed review of all operation records and process data available, the technical investigation could not reveal any evidence that the ammonia concentration of the scrubber liquor has exceeded a level of 2.5 wt-% (at least not within the last 24 hours prior to the incident).

There was always sufficient inflow of fresh demineralised water diluting the scrubber liquor which kept the ammonia concentration in the gas phase safely below the lower explosion limit for ammonia/water/air mixtures.

It could also be ruled out with high probability that an explosive gas mixture has been returned from the road tankers loading aqueous ammonia solution at the time of the incident.
In addition, the technical investigation revealed that the possible presence of hydrogen inside the scrubber tank C1301 was neglected during the process design review for the new installation as all the liquid streams entering into C1301 were considered as pure ammonia/water streams. This assumption is basically incorrect.

As part of the revamp of the ammonia plant in 2006 a process modification was executed which allowed to send the aqueous ammonia bleed from the two purge gas recovery units to the old scrubber tank C1301 (previous installation which got replaced in 2009). This stream contained up to 600 ppm hydrogen (as per vendors material balance) and was directly flashed from a pressure level of 130 bar into C1301 releasing the dissolved hydrogen. An intermediate flash vessel upstream the aqueous ammonia scrubber tank to remove the main part of the entrained hydrogen was not installed.

The detailed review of the operating records confirmed that this hydrogen containing bleed stream from the purge gas recovery units was cut-off as per sequence of events. However, the design of the scrubber tank C1301 allowed for significant dead zones underneath the flat roof in which hydrogen could have accumulated up to its vapour pressure limit in ammonia/water/air/hydrogen mixtures exceeding its lower explosion limit.

Summarizing the findings from the detailed evaluation of the process and the actual operation of the installation it was concluded that

- an explosive hydrogen-air mixture was still present in the gas phase of the aqueous ammonia scrubber tank during the time of the thunderstorm and
- lightning struck the installation at the time of the incident causing an electric arc inside the C1301 tank. The lightning strike has been reported by more than one eyewitness and is believed to be the most probable ignition source.

The following two chapters provide further verification for this incident scenario.

**Verification of hydrogen/air explosion**

Additional explosion calculations have been performed for both explosion scenarios by Yara’s central HESQ-group to clarify whether the assumed incident scenario is plausible and to potentially rule out an ammonia/air explosion.

Based on the results of these calculations it can be concluded:

- **Hydrogen/air explosion scenario:**
  The pressure build-up can be quite high even with small hydrogen quantities. Certainly the overpressure would be enough to rupture the aqueous ammonia scrubber tank.

  Using the same assumptions as taken for the rupture pressure calculations it was estimated that the ignition of a total quantity of somewhat less than 0.3 kg of hydrogen would have sufficed to exceed the maximum tolerable pressure of the scrubber tank.

- **Ammonia/air explosion scenario:**
  The ignition of an explosive ammonia/air mixture would have also resulted in a sufficient pressure build up to rupture the aqueous ammonia scrubber tank. In this case a quantity of some 2.0 kg of ammonia would have been required in order to reach the rupture pressure of 0.7 bar(g).

- **Ignition energy:**
  The ignition energy for an hydrogen/air mixture is about 0.02 mJ and over 100 mJ for an ammonia/air mixture. Thus an hydrogen/air mixture is far easier to ignite.

  In case of a lightning strike the discharged energy will be quite high, providing sufficient energy to ignite both explosive gas mixtures.
Verification of lightning strike

As part of the technical investigation the top of the scrubber vent stack as well as the earthing lug were cut out and sent to Yara Materials Engineering Porsgrunn for investigation. The objective was to determine whether these parts showed any indication of a lightning strike or overheating caused by exposure to high electrical current.

The examination revealed the presence of a fresh arc strike at the top of the vent pipe which could possibly have been caused by lightning. However a final verification is not possible.

The analysis of the earthing lug did not reveal any signs of overheating or any other indication of an exposure to extreme electrical current.

Evaluation of lightning/earthing protection in place

ATEX classification

The risk assessment performed to define the hazard area classification for this installation did not consider aqueous ammonia solutions below 30 wt-% concentration. This was based on the fact that aqueous ammonia solutions below 30 wt-% concentration are classified as non-flammable and the presence of hydrogen was not taken into account. Consequently the scrubber tank C1301 and the scrubber column have not received an ATEX classification.

Despite this, all instrumentation installed on C1301 was actually certified for the use in hazardous areas (EEx-certified as per Yara standard).

Lightning protection in place

The evaluation of the actual level of lightning protection in place revealed that the affected structure was not safely located within the lightning capture area of the surrounding installations/structures and hence was exposed to the risk of direct lightning strike.

However, following the hazard area classification (ATEX), scrubber tank and scrubber column were not categorized as an installation requiring a dedicated lightning protection system.

Equipotential protection in place

As part of the technical investigation the adequacy/technical standard of the actual earthing protection in place has been reviewed.

Based on this review it was concluded that

- all individual equipment items incl. scrubber+aqueous ammonia scrubber tank were adequately earthed except for the support structure for the scrubber column (resistance measurements of the meshed earthing showed normal values of maximum 0,04 Ohm) and
- a suitable equipotential connection of all earthing points has been put in place.

However, the support structure for the scrubber column was not earthed at all as it was probably forgotten during field erection of the new installation.

This is a significant shortcoming though it is not believed that it would have prevented the incident nor reduced its impact.

Conclusions and learning

The technical investigation of the explosion of the aqueous ammonia scrubber tank at Yara Italia, Ferrara concluded on the following root cause of the incident:

- Explosion of a trapped hydrogen/air mixture which had accumulated in dead pockets in the gas phase of the aqueous ammonia scrubber tank C1301.
  The most likely incident scenario was that the explosive mixture ignited due to a lightning
strike to the installation resulting in the over-pressure scenario.

Contributing factors to the incident:

- The design of the aqueous ammonia scrubber tank allowed for gas to be trapped and accumulate (especially due to its flat roof with only one central DN 400 gas outlet).
- The process design review for the affected installation was inaccurate/incomplete and hence the HAZOP performed during the engineering phase did not reveal/address all process risks.
- Especially the older process modification which provided the possibility to send hydrogen containing aqueous ammonia solution from the purge gas recovery units into scrubber tank C1301 was not adequately reviewed. The mandatory Management of Change process was not fully adhered to.

From this explosion incident at Yara Italia, Ferrara the following key learnings have been drawn:

1. If hydrogen is introduced into an atmospheric storage tank (either with an aqueous ammonia solution stream or via a vapour return line) and provided it has the possibility to accumulate, the hydrogen concentration in the gas phase will eventually reach the explosive limits for hydrogen/air mixtures.

2. The gas phase in atmospheric tanks containing aqueous ammonia solutions can exceed the lower explosion limit for ammonia/H2O/air gas mixtures with a minimum ammonia concentration in the liquid phase of 5 to 10 wt-% depending on its temperature. Still the risk level is relatively low as an ammonia/H2O/air mixture is quite difficult to ignite.

In principle three options exist to manage this explosion risk:

- Design the equipment so that explosive mixtures cannot accumulate
- Provide sufficient safety protections to prevent the formation of an explosive gas mixture such as a nitrogen purge. Any nitrogen purge must maintain a minimum positive pressure inside the tank under all operating conditions to be effective. Simple nitrogen blanketing does not suffice.
- Alternatively the presence of an explosive gas mixture is accepted. In this case it has to be ensured that all possible ignition sources are eliminated in accordance with the applicable electrical code (such as ATEX). An hazard area classification can (most probably) be restricted to the inside of the tank and a certain area around the release point from the vent stack. In this case the installation of a dedicated lightning protection system is highly recommended (even if not required by the applicable electrical code).

References