The Rupture of a Liquid Ammonia Storage Tank Study

The sudden increase in pressure of a 20,000 ton liquid ammonia storage tank caused the roof to shell connection to rupture and the spread of ammonia vapor on the 8th of August 2011 in Pardis Petrochemical Company in Assaluyeh port, Bushehr, Iran. This incident could have resulted in serious danger in the Pars Special Economic Region, and been followed by numerous regional and nationwide effects. Fortunately, because of unique characteristics in the design of this type of storage tank, this did not occur and its effects were limited to the spread of ammonia vapor in the amounts of approximately 30-100 ppm in the region’s atmosphere in a radius of approximately one kilometer in the direction of the prevailing wind, and resulted in no significant human loss or injuries. A close study of the incident to the liquid ammonia storage tank in this plant led to the understanding of new principles and experiences in the methods of operation and safety issues of this type of tanks, which may prevent the recurrence of similar incidents in the future.

Key words: liquid ammonia storage tank, warm ammonia product, Over Pressure, ammonia gas leakage, frangible joints

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Introduction

Pardis Petrochemical Complex, with two units of Ammonia (Licensed with M.W.Kellogg), each with a capacity of 2050 tons per day, and two units of urea (Licensed with Stamicarbon), each with a capacity of 3250 tons per day, is situated on a site with an area of 64 hectares, 270 kilometers southeast of the Bushehr port in the Pars Energy Special Economic Zone in the Assalouyeh Port, Iran. This plant contains three liquid ammonia storage tanks, each with a capacity of 20,000 tons, with an overall capacity of 60,000 tons.

The ammonia tanks are double integrity cup in tank type with perlite insulation in annular space. These storage tanks transfer their stored ammonia, through a 14 inch line with a length of 2000 meters, to the sea export terminal, Pars Port in Persian Gulf.

On Monday morning the 8th of August, 2011, between the hours of 5:34 and 5:36 a.m., the internal pressure of one of the ammonia storage tanks in this plant (TK-4501A) suddenly increased, leading to the rupture at two points in the dome roof to shell joints and the release of ammonia gas to the atmosphere. This increase in pressure also caused the folding and sinking in
some other parts of the shell at the connections to the dome roof.

Fig. 1: Ammonia vapor jet visible in the rupture point in the northern section. The Picture was taken 2 hours after the incident, 8th of August, 2011, 7:30 am

The tensions caused by the increased internal pressure of the tank was followed by the elongation and deformation in some of the nuts and bolts connecting the external shell to the concrete bottom, and caused the detachment of one of the bolts.

The spread of ammonia gas in the area resulted in the announcement of an emergency situation in the Pars Energy Special Economic Zone, and the evacuation of the non-operation personnel and employees in some of the neighboring petrochemical complexes in the early hours of the incident.

At 6:43 a.m., (about1:07h after the incident) with the announcement of the occurrence of the incident by the night shift supervisor to the safety department, the safety and fire station forces of the complex, and then the Pars Special Economic Zone arrived on location and spread the water with stationary and mobile water monitors. The spraying of water began on the damaged areas of the tank with leaking ammonia vapor and especially the northern part, in order to reduce the rate of spread of ammonia gas, and prevent the collection of gas and the formaition of ammonia cloud. The ammonia vapor jet was visible from the northern side of the place of rupture, with a length of 5 meters. Based on initial estimates, the radius of the spread of ammonia gas was about 1000 meters at the most with an amount of 30 – 100 ppm ammonia vapor concentration.

Fig. 2: TK-4501A during construction – March 2003

The pressure of the damaged tank, after the incident, was stable at 4.3 kpa (0.623 psi), and the ammonia gas jet was perfectly visible in the northern section of the tank. Considering the rupture and leakage only is in the upper section of the tank and lack of seriousness in the smell and breathing effects of the ammonia gas inside the complex, only non-operation employees were moved to the safe areas inside the complex, and the operation forces took extensive actions towards bringing the situation under control.

Considering that the conditions and the methods of start up the ammonia synthesis section and the operators’ errors played a significant role in the sudden increase in pressure and the occurrence of the incident, the method of ammonia synthesis section start up, conditions of the ammonia plant and the storage tanks in the minutes prior to and during the incident are explained.
1. Specifications of TK-4501A
1.1 Tank Type: Double Wall (Cup in) Tank with Suspended Ceiling and Dome Roof
1.2 Capacity: 20,000 Metric Ton
1.3 Ingredient: Liquid Ammonia @ -33°C (-27.4 °F), 99.8% concentration, (0.2% Water)
1.4 Design Temperature and Pressure: -40°C, 10 kpa
1.5 Manufacturer: Toyo Kanetsu K.K, Japan
1.6 Internal Diameter: 44 m
1.7 Maximum Height: 30.2 m
1.8 Insulation: Loose Perlite in Annular Space of the tank

2. Safety Systems of TK-4501A
2.1 Process Refrigeration Compressor:
   Suction Capacity from Tank: 1700 kg/hr
2.2 Pressure Control Valve: PV-4504A, Evacuated Capacity 1250 kg/hr (Setpoint: 5 kpa)
2.2 Pressure Safety Valve: PSV-4502 A1/A2, Relieving capacity: 7872 kg/hr (Setpoint: 9.8 kpa)
2.3 Two Vacuum Breaker Valve: SVB-4501 A1/A2.Max.flow:1175m³/hr, (Setpoint:-0.00065 kpa)
2.4 Flare-4501: 2500 kg/hr

<table>
<thead>
<tr>
<th>Inner tank</th>
<th>Outer tank</th>
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<tr>
<td>Service</td>
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<td>Max. Boil-off rate</td>
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<td>Plate</td>
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<td>Hydrostatic test level</td>
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Table 1: Tank Design Condition
3- Scenarios taken into consideration in the design of the safety pressure valves in TK-4501A

In the design of the pressure safety valves (PSV) of the Pardis anhydrous ammonia storage tanks (TK-4501A/B/C), three conditions that result in the sudden increase in pressure resulting from the amount of ammonia vapors produced inside the tanks have been taken into consideration by the tank designer (Toyo Kanetsu K.K CO., Japan). Based on these scenarios and the highest quantity of ammonia gas produced for the worst case for each, the PSVs were sized and selected. Required relieving capacity for PSVs shall be determined for the following combinations of Case 1, Case 2 and Case 3 whichever is larger.

Case1: Tank Boil Off (Heat in-leak) + Vapor displacement during filling

Case2: Tank Boil Off (Heat in-leak) + Drop in barometric pressure + Vapor displacement during filling

Case3: Tank Boil Off (Heat in-leak) + Boil off due to fire exposure

As it can be observed, among the scenarios considered for the sudden increase in pressure in the liquid ammonia storage tanks, the cases of unusual sudden increase in pressure resulting from the influx of produced ammonia with unsuitable temperature, and also the transfer of high volume of ammonia vapors from the ship during the loading of ammonia, and other similar cases, have not been taken into consideration. The experience from the occurrence of this incident and the importance of any incident and the dangers from the leakage from these tanks is an indication of the fact that the foreseeing of such cases is very important in the design of pressure release the safety systems in the liquid ammonia storage tanks.

| Relieving Capa. (kg/h) | 7,872 |
| Calculation Formula | API RP520 Part 1 para. 4.3.3 formula (5) |
| Fluid | NH₃ |
| Set Pressure (kpa) | 9.8 |
| Inlet Pressure (kpa) | 9.8 \times 1.1 = 10.8 (10\% accumulation) |
| Back pressure (kpa) | 99371 kpa |
| Molecular Weight | 17.0 |
| Ratio of Specific Heat | 1.31 |
| Relieving Temp. | -33.3 °C (-27.92 °F) |
| Compressibility Factor | 1.0 |

Fig. 4: Image and Specification of Pressure Safety Valves, Flow Capacity (one valve)

Fig. 5: The damage of shell to roof joints at both side of the TK-4501A
4- The operation conditions of the unit during the start up of the ammonia refrigeration section leading to the incident

The ammonia unit operators of the phase 1 of Pardis Petrochemical Complex decided to shut down the ammonia synthesis section on Saturday morning August 6\textsuperscript{th}, 2011 at 11:57:00 (36 hours prior to the incident), due to the leakage of gas from the \(\frac{3}{4}\) inch line related to the instrument equipment (TG-30106B) that was located on the outlet line from the molecular sieve bed (R-3002B). The operators isolate the system, dropping pressure on the molecular sieve and purging it with nitrogen to prepare it for the repair work required for the leakage. The repair work continued on the next day Sunday, August 7\textsuperscript{th}, 2011, and after finishing the repair work during the night shift of the same date, the ammonia unit was prepared to start up.

The startup ammonia synthesis compressor started at 1:41:31 a.m. on Monday 8\textsuperscript{th} of August, 2011 from the zero speed. The ammonia refrigeration compressor was started at 3:47:00 a.m.

The production of ammonia began at 4:52:00 a.m., and at 5:01:00 a.m. and the produced ammonia was collected from the first ammonia collecting drum D-3004 towards D-3005, and from there, it was sent towards the refrigeration package (E-3013) drum number 4 (D-4) through the control valve FV-3019. In this hour the speed of the ammonia refrigeration compressor was 6662 rpm, and the temperature of drum E-3013-D1; (TI-3038) was -26 degrees centigrade. The ammonia was almost suitable to send to TK-4501A. The standard temperature is -33 degrees centigrade.

The high pressure steam pressure (HHPS) at 12 kpa (120 barg) reduced in the pressure due to special conditions of startup at this stage in the ammonia unit. The HHPS dropped due to the simultaneous increase in the load of both synthesis and refrigeration steam turbines, the increase in the consumption of HHPS steam by the turbines in these machines, and the lack of suitable steam production in the group of E-3011A/B/C steam generators until the stabilization of the process conditions in the ammonia synthesis reactor, beginning at 5:07:00 a.m. Due to non-sufficient HHPS steam for the driving force of the turbines, the operators in the control room took steps towards reducing the rpm of the refrigeration compressors, following which the temperature in the E-3013 (D-1) increased to -14 degrees centigrade. According to design, the temperature of this drum should be -33 degrees centigrade at the time of transfer of ammonia to the storage tanks.

![Fig. 6: A view of the FCS control sheet related to the compressor and drums (E-3013 D1-4) of the ammonia refrigeration package and the pumps (P-3003A/B/C) transferring the produced ammonia towards the storage tanks.](image)
4-1 Operation conditions of the ammonia plant in the minutes before the incident

Up till 5:31:00 a.m. the transfer of ammonia from the ammonia flash drum D-3005 to D-4 (E-3013) was taking place continuously. At this moment the flow from this path was cut off, and the transfer of ammonia directly to D-1 (E-3013) was done by the control room personnel.

This action was done to increase the level of the D-1 to 50%. This action was very rapid and operator then was neglected to monitor this section and control the consequence effects of the action. At 5:32:00 the amount of transfer flow from D-3005 to D-1 (E-3013) via the control valve FV-3020 reached its peak, equivalent to 112 m³/hr and then continued in fluctuation.

The level of ammonia in D-1 increased rapidly and rose from 6% to 63% by 5:38:00. Considering that the set level of the controller of this drum was automatically at 50%, after its ammonia level reached 50% at 5:34:16, the transfer of ammonia to TK-4501A via the control valve LV-3022 began. At this situation the temperature of D-1 was at -12 degrees centigrade and in unsuitable conditions for transfer.

The flow of transferred ammonia, beginning at this time, continued for 2 minutes, steadily rising, reaching 70.41t/hr at 5:36:16 and after a drop of about 3 t/hr continued its rise to 115.05 t/hr at 5:42:16.

The numerous control room personnel errors committed in this section are listed as below:

1) The quick transfer of the produced ammonia from D-3005 towards E-3013D-1
2) Inattention to the temperature of D-1
3) Putting to service of P-3003 pumps sooner than normal
4) Lack of sufficient attention to the fast rise in the level of D-1 and the transfer of ammonia with unsuitable temperature and flow towards TK-4501A
5) Lack of determination of the real cause of the ammonia tank pressure increase
6) No appropriate action to stop the flow of produced ammonia towards TK-4501A
7) Unnecessary force of complex manager for ammonia production until the morning which cause the severe stress on the night shift control room personnel

4-2 The conditions of TK-4501A and other two ammonia storage tanks (TK-4501 B&C) at the moment of the incident occurrence

Due to the ammonia refrigeration compressor (C-3002) being out of service in the phase 1 ammonia unit, because of the conditions of the starting up of the unit and lack of receipt of ammonia vapors from the storage tank, the pressures of all three tanks before the incident were approximately 74 mbar, which is considered a high pressure.

Because the PCV's set points had been increased to 75 mbar against the procedure for preventing lost of ammonia vapor, the PCV's and flare were not operating at this moment. According to the design, the normal pressure in these liquid ammonia storage tanks is equivalent to 50 mbar.

The phase 2 ammonia unit of the complex, which based on design has the capability of receiving ammonia vapors from the storage tanks, due to instruments problems in its ammonia refrigeration compressor (2-C-3002), and in order to prevent the fluctuation in the speed and shut down, had not received ammonia vapors from the storage tanks for months before the occurrence of the incident.

The related valves were in a shut-off position. Both the emergency refrigeration screw type compressors located in the storage tanks dike had the role of receiving the ammonia vapors at the times when the refrigeration compressors of the ammonia units were out of service.
These compressors were also out of service due to repair problems.

The pressure in TK-4501A began to rise at 5:35:57, and reached its peak of 312 mbar at 5:37:48. Also, from the beginning of the rise in the pressure of the tank, Suspended Deck differential pressure was created. At the peak point the amount of pressure above the Suspended Deck was equivalent to 31.2 kpa (312 mbar), and the amount of pressure below it was equal to 218 mbar. The pressures in the TK-4501B/C then had an ascending trend and reached a peak level of 9.6 kpa (96 mbar) at 5:39:00 and 5:41:00 respectively, and had a downward trend from then on.

5 – Examination of the main operation negligence creating the conditions for the occurrence of the incident

The approximate weighing of the main causes leading to the damage in the tank was done based on an overall engineering sense of the effective parameters on the incident.

5-1 Human error in the transfer of produced ammonia with unsuitable temperature and high flow towards the TK-4501A storage tank (Approximate quantity of effectiveness: 70%)

The quick transfer of ammonia from D-3005 towards D-1 (E-3013) followed by the transfer of ammonia from D-1 (E-3013) towards TK-4501A with flow and temperature higher than that designed led to the very quick rise in the pressure of TK-4501A.

Considering the fact that the urea unit was in service, the ammonia produced could have been transferred to this unit as warm feed and after the temperature of D-1 (E-3013) was made stable and suitable, the transfer of cold ammonia to the storage tanks begun as the standard procedure of ammonia plant startup. This was a part of standard procedures for ammonia startup, and the operators were trained to recognize this situation.
5-2 The unsuitability of the temperature and thermodynamic conditions of the produced ammonia transfer line to the storage tank (15%)

The pressure in the ammonia storage tanks, at the time of the incident, was equal to 7.4 kpa (74 mbar). Considering that the XV-4503 valve, the connecting valve between the produced ammonia line and TK-4501A was open the pressure of the line was equivalent to that of the tank.

In the ammonia units of the Pardis Petrochemical Company, the amount of water about 0.2% by weight is added to ammonia product in order to prevent the SCC type corrosion in the ammonia storage tanks, liquid ammonia loading lines and also the storages in the ammonia exporting ships. After shut down of ammonia synthesis section on Saturday 6th August, 2011, due to the error of the site operator the injection water valve was left open. It is foreseen that with the entrance of near 5 cubic meter water into the line and its mixing with the remaining ammonia in it, an exothermic reaction of ammonia water took place leading to the evaporation of part of the liquid ammonia in the line.

Fig. 9: The form of damage in the southern section of TK-4501A

Fig. 10: The form of the damage in the northern section of TK-4501A

The collection of these factors created conditions of 700 meter line of ammonia product from the outlet of the produced ammonia pumps to the inlet of TK-4501A to not have suitable temperature conditions and take a two-phase form. The transfer of ammonia with
unsuitable temperature and very high flow, as a shock, also acted as a piston and transferred the two-phase fluids present in the line towards the tank. This fact caused the sudden increase in pressure beyond the venting capacity of the pressure safety valves of the tank followed by the rupture in the shell and roof and the leakage of ammonia from it.

5-3 The being out of service of the emergency refrigeration compressors receiving ammonia vapors due to maintenance (15%)

Both of two electrical emergency refrigeration compressors are installed on the tanks farm in order to maintain the tank pressure steady at times when the main refrigeration compressors of each of the ammonia units are tripped, were out of service for various maintenance reasons. If these compressors were in service, there was a possibility to damp the pressure rising and avoid the incident.

6- Investigation on the deformation and damage of TK-4501A

The transfer of ammonia with unsuitable temperature and high flow caused a quick rise in pressure in TK-4501A and also a difference in pressure between the space above and below the suspended deck.

Due to the high speed and strength in the occurrence of this incident and also the approximate simultaneity of the time of complete opening of the pressure release control valve (PV-4504A) towards the ammonia flare tanks by the control room personnel with the set amount of pressure safety valves (PSV), the exact time of operation of these valves is not traceable by the pressure registering curves. Therefore, this 10 second time span in the stoppage of increase in pressure below the suspended deck can be analyzed as the possible time of operation of the tank’s pressure safety valves.

Also, regarding the analysis of the 10-second time span in the stabilization of the trend of increase in pressure below the suspended deck, stabilization and reduction of about 3 t/hr of the transfer flow to the tank for a few seconds at 5:36:16 was not without effect either. Following the testing of the two pressure safety valves of the tank in the central mechanical shop of the complex, it was concluded the valves had properly functioned at their set operating levels.
Considering the existence of second-curves of the tank’s pressure in the moments before the damage, the internal pressure of TK-4501A never dropped below the atmospheric pressure and after a downward trend was stabilized at approximately 80 mbar. Therefore, the evidence indicates that a vacuum did not form for the damaged tank.

Considering the 312 mbar pressure exerted on the dome roof, and also the creation of pressure difference of approximately 94 mbar between the spaces above and below the suspended deck, and considering the connection of the dome roof to the suspended deck through hanger supports the resultant force was towards the dome roof of the tank. The internal tension pressure resulting from the tendency of the dome roof towards upward movement and the tension in the external layer of the tank caused the sinking in the connecting region of the dome roof to shell at two points and also damage and deformation of a major part of the dome roof and the upper section of its shell.

7- Operation of controlling the leakage of ammonia vapors from the damaged points in TK-4501A

After the incident the leakage control team formed by the safety and maintenance units performed the close inspection of the damaged points having ammonia leaks using complete safety equipment, crane and basket. After identifying the exact positions of the ruptures in the shell of the tank and necessary measurements, through a creative design by the maintenance crew, three clamps were designed and constructed in the central workshop of the complex and installed on the areas having leakage.

These operations were performed within 27 hours of the incident and at 9:00 a.m. Tuesday morning August 9th, 2011, with installing three clamps on the damaged areas the leakage of ammonia vapors were brought under control.

8- Comparative examination of the TK-4501A incident with similar incidents in the world

According to the reports of American Institute of Chemical Engineering (AICHE), from 1965 to the end of 2011 twenty six incidents have occurred related to the liquid ammonia storage tanks. For a better understanding of the damage to the TK-4501A ammonia storage tank and the affecting parameters in the occurrence of such incidents 40 incidents in connection with stationary and mobile liquid ammonia storage tanks, ammonia water, and ammonia gas under pressure and the circumstances leading to their incidents were examined and studied. Thirty-seven cases of the incidents were related to the stationary and mobile liquid ammonia tanks with capacity of 10-20 tons or ammonia gas under pressure. Three incidents in large scale ammonia storage tanks are as below:

1) Rupture of cryogenic ammonia tank, March 20th 1989, Lithuania (USSR)
2) Ammonia tank incident, Geismar, USA, October 2th, 1984.
3) Ammonia tank incident, Rostok, Germany, January 4th, 2005.

Fig. 13: Sample of the clamps manufactured creatively, using cold insulation
Although the other 37th incidents were occurred contained considerable points with respect to matters of operation, maintenance and safety, and in some cases lead to vast human incidents, with respect to the storage capacity and dimensions, they are not comparable to the stationary storage tanks with high capacity for storing ammonia.

8-1 The Roll Over phenomenon

The point of entry of ammonia to the ammonia tank in Lithuania was to the lower section of the tank. This point can increase the time span between the transfer of ammonia at unsuitable temperature and its vapor release. The Roll Over phenomenon occurred when warm ammonia inlet nozzle is in the lower section of the tank. When warm ammonia had entered to the tank, the layer of heated liquid ammonia has a tendency to move upward and this fact is followed by the displacement of ammonia layers with different temperatures inside the tank. The eventual turbulence caused sudden increase in pressure inside the tank. This phenomenon has been referred to as the roll-over phenomenon in the API standards. In the results section of this case study it has been stressed that in this area, the design must be corrected and the point of entry of produced ammonia be moved to the upper part of the tank. This point was taken into consideration in the design of the ammonia tanks of Pardis Petrochemical Complex so that the Roll Over phenomenon did not occur.

9 –The examination of scientific and technical causes of the situation and the form of damage

After the incident of the damage to TK-4501A of the complex at 05:36 on Monday morning August 8th, 2011, the initial examinations showed indications of increased internal pressures of the tank to levels much higher than those in the design of the two upper and lower sections of the suspended deck. The pressure above the deck had reached 312 mbar and that of below the deck had reached approximately 219 mbar.

This took place due to the transfer of produced ammonia at high temperature and flow (-12°C &
70 -115 t/hr) and caused the overpressuring of the tank. But in images of the buckling of the tank, at first glance indicates the possibility of creation of vacuum. However, considering the existence of second pressure curves and that in no time span was this pressure below the atmospheric pressure, the possibility of the occurrence of vacuum, in the first hour of the incident, was rejected.

Fig. 15: The stretching of the nuts and bolts holding the external shell to the concrete bottom of the tank, and the detachment of one of them due to increased pressure and the resultant force exerted – The deformation in the metal bottom of the tank in that situation following its emptying and cutting for the purpose of major repair

For the purpose of identifying and justification of the manner in which the tank was damaged hundreds of pages of technical books, journals, and standards related to this matter were studied. Eventually examinations led to a key point namely the method of design of frangible joint at the point of connection of the roof to the shell of atmospheric tanks within API-620 and API-650. The continuation of the studies concentrated on this subject and the information and data obtained clarified the causes of the manner of damage in the ammonia tank of pardis petrochemical complex.

9-1 Frangible Joint Concept

Sudden overpressure can lead to the catastrophic loss of tank integrity. One undesirable mode of failure is the loss of the shell-to-bottom joints, which results in loss of containment and spillage of the contents. If the shell or bottom fails, liquids are released and the neighboring tanks and structures are in great danger of being ignited or damaged. To reduce this hazard, the frangible roof-to-shell joint is designed to fail before failure occur in the tank shell or the shell-to-bottom joint. When the frangible joint fails, the roof of the tank becomes free to move, thereby providing a large venting capability to dissipate the pressure.

The design rules for frangible roof joints of fuel storage tanks are described by the American Petroleum Institute in API 650 (API, 1993). That standard has been used or referenced in many countries. A roof-to-shell joint designed according to API 650 rules is considered to be frangible and in case of excessive internal pressure, intended to fail before failure occur in the tank shell or shell-to-bottom joints. However, practice has confirmed that a roof-to-shell joint so designed may not perform as intended, especially for smaller tanks. A means to prevent such catastrophic failure is needed by tank manufacturers as well as users.
Fig. 16: Flat Roof Tank after Test, First Large Buckling on Flat Roof Tank under 1.2 psi Pressure.

Fig. 17: Large Deformation Buckles on Large Slope Roof Tank, under 5.5 psi pressure

Fig. 18: Stitch Welded Tank after Test, Failure Occurred on Roof Plate and Top Angle, Buckling on Top Shell
9-2 Design Method of TK-4501A/B/C of Pardis Petrochemical Complex

In the design of the ammonia storage tanks of Pardis petrochemical complex the version of API-620(2000) and API-650(2000) have been used. The manner of design of the compression ring at the junction point of the dome roof to the external shell, also is consistent with the design standards sample in this area. Considering the examinations and comparisons made with the results of articles, various international studies, the existing standards and similar incidents in two cases of dents and folds in the roof and shell of the tank the following results are presented.

9-3 Two main dents in the northern and southern sections and the ruptures created

These folds in the roof and shell of the tank were done exactly according to the design made for this type of tank. Increase in internal pressure of the tank is effective at the weakest points, i.e. the connection points between the roof and the shell. Also the type and manner of sinking is consistent with the type and manner of sinking in similar incidents and with practical experiments done. The symmetry of the position of the buckling is not necessarily related to the position of the ammonia line entering the tank and in the sample experiments done in this field 90 and 180 degree symmetry or lack thereof is observed.

The creation of the damage leading to the perforation in the shell of the tank by entering hot ammonia to it, also led to the release of emergency pressure more than designated amount for 2 PSV’s and also one pressure control valve (PV-4501) and prevented damage to the shell at the point of connection of the
shell to the bottom. Of course pressure tension and stretching is exerted upon the shell and anchor bolts of the bottom of the tank.

Fig. 21: Buckling and damages in the shell and roof from the internal view of the tank (After Decommissioning, 28 May, 2012)

9-4 The folds in the roof and the upper section of the body of the tank

According to the calculation results, the simulations made in the researches under study for atmospheric storage tanks and the pictures of similar incidents in venting conditions, a twisting torque occurs in the roof and the upper section of the shell attached to the roof causing folding similar to that of TK-4501A.

10 – The Lessons learned from the Rupture of TK-4501A

10-1 Foreseeing the phenomenon of sudden pressure increase by considering a higher number of PSV’s or rupture discs

The incident of ammonia leakage from the storage tanks at Pardis Petrochemical Complex is one of the main incidents that occurred as a result of sudden increase in pressure in this type of tanks. In designing the pressure relief system of this type of tank an increase in pressure resulting from unnatural cases, such as operation and maintenance errors or other incidents as mentioned in the previous parts of this paper is foreseen such that upper parts of the shell and the roof of the tank rupture and its pressure is released. But considering the problems pursuant to ammonia vapor leakage control and the dumping of the ammonia remaining in the tank and its maintenance, it is only logical that the possibility of the occurrence of this incident is considered in the design of this type of tank with an increase in the number of pressure safety valves and the installation of rupture disks required for the dumping of high amounts of vapors. Any type of damage to the shell and roof of this type of tank can be prevented and the problems due to initial control of the leakage of ammonia vapors and their drainage and repair can be mitigated.

10-2 Change in the connection line of the ammonia vapors above and below the suspended deck

In the design of ammonia storage tanks of Pardis Petrochemical Complex the produced ammonia vapor in the space below the suspended deck is transferred to the space above the suspended deck through two 24-inch spool line. The nozzles ending in two pressure safety valves in these tanks are placed on the upper part of the suspended deck and on the dome roof. At the time of sudden increase in pressures created in these tanks, it has been noticed that, in a second’s time span difference in pressure is created in the spaces above and below the suspended deck. At the time of the TK-4501A tank this difference in pressure reached 100 mbar. This caused the damage in the layers of heat insulation between the suspended deck and the internal wall of the tank. Increase in the number of connection lines or change in the design of the method of connection between the ammonia vapor in the upper and lower sections of the suspended deck seems urgent.

10-3 Forecasting the interlocks necessary for preventing the transfer of ammonia at high temperature towards storage tanks

Considering the importance of monitoring and control of the temperature of transferred ammonia towards ammonia tanks in preventing the occurrence of sudden increase in pressure and damage to these tanks, it is necessary to foresee the required standards in this area and the creation of interlocks of instruments cutting off the flow of ammonia in case of increase in its temperature to amounts higher than standard (-33 degrees centigrade) considering all related cases of operation and safety.

10-4 Creation of warning systems, piping requirements and electrical instruments for
the purpose of preventing the entrance of water to the transfer ammonia line to the storage tank

Injection of water (return condensed from the turbine) to the produced ammonia transferred to the storage tanks for the purpose of maintaining the amount of water at the 0.2 percent by weight in order to prevent SCC type corrosion (Stress Corrosion Cracking) in the ammonia units of Pardis Petrochemical Complex is controlled through a manual valve and flow meter on the site. The absence in the control room of an indicator for the amount of flow and also a flow control valve caused the related manual valve to stay open due to the operators’ error at the time of recession of the unit from the ammonia synthesis section. The injection of water to the ammonia production line continued. This matter was followed by an exothermic reaction of the mixing of water with ammonia and the production of ammonia vapor and increase in the pressure and temperature of the line. This also occurred in the recession before the startup leading to the incident and was one of the factors effective in the unsuitable thermodynamic and fluid conditions of the transferred ammonia line and the increase in the pressure of the tank. Therefore the installation of the required instrument and piping equipment along this line and creating a connection between indication instruments with the control room is necessary.

10-5 Shortening the length of ammonia product line towards the ammonia storage tanks

Thermodynamic and fluidity status of the lines transferring ammonia to the ammonia tanks is an important factor in the safety of the transfer operations. The existence of a long path and the difference in level between the product ammonia pumps and the storage tanks causes the transfer line to remain full of ammonia at the time of shut down of the unit and non-transfer of ammonia and its rise in temperature over time causes the evaporation and creation of two-phase fluid. This volume of high temperature ammonia inside the line after the unit is put in service becomes a potential factor in the entry of a considerable amount of two-phase fluid with high temperature and increase in the pressure of the tank. The transfer of ammonia with high flow, dumps the content of the line inside the tank leading to the sudden increase in its pressure; a point which has been one of the main factors in the incident of damage to the ammonia tank in Pardis Petrochemical Complex.

10-6 The display of the values of the temperature indicators inside the tank and the installation of temperature transmitters on the line of produced ammonia

Inside the ammonia storage tanks in Pardis Complex, at 4 different levels, there are 16 temperature transmitters and the temperatures are indicated on a local panel on site. On the ammonia transfer line no temperature transmitter indicator is present. The lack of display of the temperature inside the tank in control room and the absence of temperature indicator on the transfer line of ammonia product results in the fact that there is no monitoring of these values and there exists no possibility of creation of control sense for the operators allowing preventive actions when any change in temperature is noticed. Also, the possibility of having access to archive information related to the temperature profile does not exist. Therefore, design of tank and ammonia line temperature indicators in the control room seems necessary.

10-7 The installation of leak detector system for the leakage of ammonia, monitoring cameras, and also placing special operators at the site of the ammonia tanks

Between the time of appearance of high high pressure alarm of the tank which the incident of the leakage of ammonia were occurred at 5:36 and the time of noticing by the site operator at
6:43 a.m. there was a time lapse of more than one hour. The reason for the operator taking notice was his presence at the location for the purpose of adjusting the pressure on one of the pumps transferring ammonia to the urea unit. This operator while adjusting the pressure of the pump experienced difficulty with breathing which was due to the spread of ammonia gas at the location of the ammonia storage tanks. The operator hardly managed to leave the area and report the incident. Losing more than an hour in an incident where every second counts is a considerable time where, in the event of the leakage of ammonia specially in liquid form to the environment whether in this incident or any other similar incident is a valuable time for the response of the operation forces and the evacuation of the non-operation forces, which is lost.

10-8 The importance of maintenance of the emergency refrigeration compressors and their availability

Considering the numerous problems, short and long term with this equipment becoming routine and ordinary, the malfunction of both emergency compressors at the time of the incident was another factor amplifying the unsuitable conditions leading to the incident. Therefore, special attention must be paid to routine maintenance of this equipment.

10-9 The use of simulation models of leakage and their operational use in safety scenarios

A simulation done using PHAST software by the engineers Mr. Alireza Narimannejad, Mr. Ahmad Khoshgerd, and Ms. Farideh Atabi was performed on the ammonia storage tanks of Pardis Petrochemical Complex in 2007 and was presented as the article of simulation of sudden release of ammonia from the storage tanks. The incident occurred for TK-4501A allowed this simulation to be put to practical validity test. Field observations at the time of the incident of ammonia tank of Pardis Complex and subsequent evaluations indicated that the manner of the spread of ammonia gas that had occurred was to a high percentage consistent with the leakage model forecasted for summer conditions. This fact is demonstrative of the importance of the utilization of appropriate simulation software and investment in this area. In addition, the exit information of these projects also must be implemented in practice in the safety plans and scenarios. [3]

10-10 The safety forces act with respect to the maneuvers and the performed scenarios and the special situations of ammonia leakage

Several planned maneuvers of control of ammonia leakage are held annually at the ammonia storage tank farm of Pardis Petrochemical Company due to it being recognized as a potential danger factors in Pars Special Economic Zone. These maneuvers performed internally by the Pardis Petrochemical Complex safety department or regionally with the presence of safety and fire-fighting personnel of other petrochemical complexes of the Pars region. The manner of operation of the safety and fire-fighting forces in the incident of the rupture and the spread of ammonia gas in Pardis Petrochemical Complex demonstrated that there must be special predetermined scenarios in the manner of safety operations in cases of the spread of ammonia in the form of gas or liquid. Since the majority of the safety and fire-fighting forces receive training in confronting explosions and fire their speed at evaluation, decision making, and dealing with the leakage of ammonia gas and the reaction time in the evacuation of non-operation personnel from the location is of special importance.

10-11 The installation and increase in the number of hydrant systems and water spray and sprinkler on the roof and shell of the liquid ammonia storage tanks for the purpose of preventing the formation of ammonia cloud.
Considering the experience with the leakage of ammonia and the manner of safety operations performed, the installation and increase in the number of monitoring systems for fire hydrants in the liquid ammonia storage tanks, and also the installation of spray and sprinkler systems on the liquid ammonia storage tanks seems necessary. It should be acknowledged that liquid ammonia leaks should avoid contact with water unless an overabundance of water is readily available. Adding water usually results in an increase the vaporization rate and higher ppm levels.

**Conclusion**

The rupture of TK-4501A ammonia storage tank of Pardis Petrochemical Company on the 8th of August, 2011 was mainly due to human error and the transfer of liquid ammonia at unsuitable temperature (-12 degrees centigrade), and also a very high flow (112 cubic meters per second).

Although the design of this tank prevented a major disaster and human catastrophe, the serious pursuing problems in the control of vapor leaks in the shell and roof in the damaged areas were controlled within the first 24 hours of the incident by installing 3 clamps manufactured within the complex.

The complete drainage of the tank and its placement in safe conditions took approximately 10 months. During this time, due to small ammonia gas leakage from the place of installation of clamps, the smell of ammonia and the effects of its spread exist inside Pardis Complex and in some instances depending on the direction of the prevailing wind, which caused breathing problems in the neighboring petrochemical complexes. The incident demonstrated that the training of control room operators and attention to the operation and maintenance of the liquid ammonia storage tanks, such as predictive maintenance of the pressure safety valves and new design in safety equipment is necessary for the purpose of preventing the occurrence of similar incidents.

**References**


2- American Petroleum Institute: API 620 & 650

3- Modeling of sudden ammonia spreading from ammonia tank and preparation of reaction scenario in emergency situation: A.Narimannejad, F.Atabi, A.Khoshgard, HSE Department, NPC, Iran
Annexes

TK-4501A Decommissioning and Maintenance Pictures