Explosion of Ammonia Liquor Tank

New operating procedures code was developed following a detailed investigation of the incident at an agricultural chemicals plant in England.

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An investigation of an explosion of a weak ammonia liquor tank at the Billingham plant of ICI Agricultural Division has led to a more clear understanding of causes and the drawing up of a new code of practice to avoid a recurrence of this type of problem.

When the tank exploded, all 1,000 tons of 10% liquor it contained was spilled. Part of the surrounding bund wall was demolished when the tank fell on it and another part of the wall failed. This allowed all the liquor to escape and spread over the surrounding area. The toxic emergency procedure was instituted. Four people were gassed mildly.

The tank failed because of internal overpressuring due to a relatively slow combustion of gases in the vapor space above the liquor inside. A mixture of ammonia and air containing some hydrogen and methane would have occupied the vapor space. No source of ignition was identified.

Mild steel was the material of construction of the 1,750-cu.meter tank, which was 50 ft. in diameter and 32 ft. in height. Detailed design and construction method is illustrated in Figure 1. The tank vented to atmosphere through a 6-in. I.D. vent pipe, 20 ft. long, mounted vertically at the apex of the tank roof: no relief valve or vacuum release valve was therefore fitted.

Liquor was supplied to the tank from the high-pressure water scrubber associated with ICI's Kellogg low-pressure ammonia (LPA) plants, and from a small ammonia bottling plant. The only consumer of the liquor was an ammonia recovery still. Normal flow rates to the tank were 50 ton/ day from the LPA plants and 10 ton/day from the bottling plant. Strength of the liquor varied from 10 to 20% ammonia at ambient temperatures. The still consumption was

Figure 2. Diagram of the liquor system.

of the order of 500 ton/day, and the normal mode of operation was to run the still in campaigns every 24 days or so.

At the beginning of the incident, the tank was filling up, after the still had been run 13 days previously. Figure 2 is a line diagram of the system.

On the morning of January 3,1973, the liquor tank was receiving normal run-down from the LPA plants scrubber. The rate was around 2 ton/hr. and the strength about 9% NH₃. No run-down was being received from the bottling plant.

At about 10:30 a.m., the works shift manager heard what he thought was an explosion, and the high level alarm on the liquor tank indicated. It would not cancel. It was also noted that the level was indicated as being zero whereas the level at 6 a.m. had been 960 ton and rising. The shift

Figure 1. Detailed design and method of construction of the tank.

Figure 3. View of failed tank from west of bund, looking southeast, showing demolished sections of the bund wall.

Figure 4. General view across bunded area, looking southwest.

manager was then informed that the liquor tank had exploded and that ammonia liquor was spreading on the surrounding area. He immediately initiated the toxic alarm procedure.

Several eye-witnesses reported the incident and their reports were summarized as follows:

1. A loud rumbling and roaring noise was heard.

2. The tank lifted from its base vertically and then slowly toppled over in a southerly direction.

3. A large ball of orange-red flame was seen being emitted from the base area of the tank for several seconds—5 at the most.

4. The area around the tank compound was filled with greyish/white smoke following the collapse of the tank; and smoke in particular was seen being emitted from the 6-in. atmospheric tank vent.

Final position of tank reveals some helpful facts

The resultant position and appearance of the tank is shown in the photographs in Figures 3, 4 and 5. The evidence indicated a rupture of the side wall of the tank from its base, a movement of the tank in a southerly direction, collapse of the tank on the south bund wall section, and the removal of a section of the bund wall from the west side. The latter is thought to have been caused by either weight of ammonia liquor or—more likely—by the concrete steps attached to the tank stairway colliding with the wall and knocking a section out.

The basic modes in which a tank can fail were considered to be:

1. Mechanical failure *per se,* under normal working conditions.

2. As a result of internal over-pressuring without sufficient relieving facilities.

3. As a result of internal under-pressuring without vacuum-breaking facilities.

4. As a result of damage brought about by some external agent.

Mechanical failure was ruled out, as the tank would not have failed in the way it did; that is, a weld seam failure

Figure 5. Close-up of failed tank from the east side. The probable sequence of events during the failure was as follows. The initial failure of the base-to-wall seam occurred on the north side of the tank and ran around to the south side in both directions. This caused the north side of the tank to lift most, and the effect of the pressure in the tank was to eject the liquor through the split seam, and to push the tank in the opposite direction. Therefore, the tank virtually pivoted about its south side base seam (the final separation of the split seams was only about two feet) and fell onto the bund wall. The weight of the unsupported north side of the tank wall then caused it to collapse inwards, resulting in the final appearance shown in the photographs here.

would have been expected rather than total removal of the tank from its base.

Internal over-pressure was virtually certain to have been the cause of failure. The dished appearance of the tank base indicated that on initial over-pressuring the tank began to "inflate," or attempt to attain a spherical shape, and then failed along the weakest point—the base-to-wall joint in this tank. A pressure of 30 lb./sq.in. gauge would probably have been required to bring about failure.

There was no evidence of either implosion or external damage.

It was considered that over-pressuring of the tank could arise by one of the following five mechanisms.

1. By hydraulic head as a result of incorrect level indication associated with the 6-in. vent being blocked. Mass balances and inspection of the pipe eliminated these as possibilities.

2. By sudden generation of large gas volumes in the tank as a result of the ingress of anhydrous ammonia. No evidence of this occurring was found.

3. By the "rollover effect" whereby introduction of liquor at the bottom of the tank could give rise to the formation of a layer of warmer, lower-density liquor beneath a colder denser layer. The layers suddenly roll over and evolve large volumes of gas because of the sudden pressure release above the warm liquor. This could have occurred in this case but the amount of gas that would be formed in such an'instance would be nowhere near the capacity of the vent pipe (about $25,000$ Rcu.m./hr. before tank failure).

4. By gas break-through into the feed line to the tank. Since a full gas break-through would only give about 1,800 cu.m./hr. of gas escaping to the tank, the vent would easily cope with this. Moreover, there was no evidence of this having happened.

5. By combustion in the vapor phase. All the evidence pointed to this as the most likely cause. Combustion gas and air would be present as a result of the mode of tank operation: the gas would contain hydrogen and methane as well as ammonia as a result of desorption from the feed liquor originating from the LPA scrubber—about 6 Rcu.m./ hr. of hydrogen and methane.

Search for cause of ignition

The problem was to find a source of ignition. These can be divided into sensible heat sources, and sources of energy giving sparks, which are either mechanical, electrical or chemical.

Sensible heat sources were discounted because no work involving flames or sparks was being done on the tank nor in its vicinity at the time of the incident.

There were no mechanical sources of energy that could give a spark in the vapor space in the tank (creation of sparks by metal/metal contact during tank failure implies some other source of initial tank over pressuring which has already been ruled out).

Electrical sources can be divided into current and static electricity.

The only possible electrical contact with the tank vapor space was the high level alarm. This consisted of a stainless steel tube containing a magnetic switch activated by a float free to slide up and down the tube. A thorough inspection after the explosion revealed absolutely no fault which could have given rise to a spark. Other electrical supplies to the tank area were examined, and no faults were found other than obvious mechanical damage brought about by the tank failure. Current electrical faults were therefore eliminated as a cause.

Static electricity could have resulted from liquid movement in and out of the tank, and of vapor release from the atmospheric vent. The feed inlet is at the bottom and normal input is very low, thus any associated charges would be extremely small. Certainly no spray electrification could have occurred. Ammonia liquor is heavily ionized and hence a strong conductor, so that any charge would quickly run to earth.

The only protrusions into the vapor space of the tank were the level indicators and the high level alarm. There was no indication of these not being in perfectly good electrical contact with the tank and they were not of a shape conducive to retaining a high charge.

It was just conceivable that had a full gas break-through from the LPA scrubber occurred (1800 Rcu.m./hr.), the relatively high gas velocities in the vent (about 90 ft./sec.) that would result could either generate a charge to ignite the gas if it contained significant quantities of hydrogen or break off rust particles and cause friction sparks with the same result. However, there was no evidence of breakthrough, therefore this theory cannot really be substantiated.

There was no record of any atmospheric static on the day in question, the weather being damp and misty.

Chemical sources were thus reached by a process of elimination. Although no direct evidence was found, they cannot be completely discounted. A likely substance would be pyrophoric catalyst dust. This would somehow have to be deposited on the walls of the tank and then dried out. Analyses revealed no evidence of dust in the incoming stream. It is known from a literature survey that ferrous sulfide deposition on tank walls and spontaneously decomposing has caused explosion; however this can also be discounted because no source for ferrous sulfide existed.

General observations and summary

This incident is unusual in that no process abnormality appeared to occur at any time before or during the incident, nor was any sort of malfunction or failure noted. It seems to have been simply a very small chance occurrence, the danger of which could possibly have always been present.

Ammonia liquor has been stored on the Billingham site and at other sites in the Agricultural Division for about 40 years, without any similar incident. Only four incidents of explosions in liquor tanks anywhere have been traced. Of these, two were due to local heating from welding and the other two were due to ferrous sulfide decomposition. In both the latter cases, the cause could not be proved but presence of large quantities of sulfide put the matter beyond reasonable doubt. The major cause for explosions in *any* sort of tank is static. However, as explained above, this is not thought likely to be the cause here.

It was concluded that the tank failed because of the combustion of gases in the vapor space of the tank, but that the necessary source of ignition could not be identified. Because of this, a new Code of Practice was devised to cover all likely possibilities.

The Code of Practice is too lengthy to discuss here in detail but includes as main points:

1. If hydrogen can be present, then gas blanketing must be used. The blanketing gas most commonly used would be nitrogen.

2. The roof-to-wall joint should be weaker than the wall-to-floor joint so that in the event of over-pressuring, the roof fails: this was *not* the case in the incident described.

3. All possible sources of ignition should be eliminated. In particular, the tank should be fully earthed, and any associated electrical equipment should not be capable of initiating an explosion. The tank must be designed to eliminate the likelihood of static discharges.

4. Pressure-vacuum relief valves should be fitted if the partial pressure 'of the ammonia over the liquor can reach 0.75 bars (27% liquor at 25°C). *#*