Cryogenic Storage of Anhydrous Ammonia

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As well as providing bulk cryogenic storage for LNG and LPG, TGE-Gas is getting an increased number of projects, and project enquiries for large scale cryogenic bulk storage of anhydrous ammonia. Ammonia has long been used in the fertiliser industry, but it now has the potential to be a clean feed for production of hydrogen gas fuelling aviation. This will lead to an increase in the need for cryogenic anhydrous ammonia bulk storage tanks at new locations such as airports.

Hazards 32 delegates will benefit by understanding the properties of anhydrous ammonia that make it very suitable for cryogenic bulk storage at atmospheric pressure and will gain an understanding of how the hazards from liquid ammonia can be successfully managed during commissioning and operation.

TGE

As well as providing bulk cryogenic storage for LNG and LPG, TGE-Gas is getting an increased number of projects, and project enquiries for large scale cryogenic bulk storage of anhydrous ammonia. Contracts completed to date have included:

- FEED and EP +CS terminal project for a 25,000 tonne full containment anhydrous ammonia bulk storage tank, ship loading and unloading system, send-out pumps and boil off gas handling system for Gübre Fabrikalari T.A.S.in the Izmit region of Turkey;
- EPC terminal project including 2 x 30,000 m^3 double containment tanks, jetty ship unloading/loading system, in-tank pumps , blow down and flare system and BOG handling system for Formosa Petrochemical Corporation in Mailiao, Taiwan
- FEED and EPC storage facility project for 2 x 5480 m^3 pressurised anhydrous ammonia spheres each having 3,000 tons capacity, compression system (with all peripherals) for the operation of the spheres, ammonia and syngas flares, send-out pumps and start-up pump for Eti Bakir in Mazidagi, Turkey;
- FEED and EP +CS terminal project for a 15,000 tonne full containment anhydrous ammonia bulk storage tank plus ship unloading and send out services and boil-off gas handling system for Eti Bakir in Samsun, Turkey;
- FEED and EP +CS for a further 15,000 tonne full containment anhydrous ammonia bulk storage tank and boil-off gas handling system for Eti Bakir in Samsun, Turkey;

Ammonia – Production and uses

Ammonia has long been used in the fertiliser industry, but it new markets are now appearing in the energy sector.

Originally processed from processing bird guano, gaseous ammonia is now mainly produced industrially by reacting hydrogen and nitrogen over a finely divided iron oxide based catalyst at high temperature (over 400 ^{o}C) and pressure (over 100 barg). This reaction is known as the Haber-Bosch process, discovered by German scientists Fritz Haber and Carl Bosch early in the 20th Century. The modern day high-pressure ammonia synthesis process is essentially the same, but the energy consumption of about 100 GJ/tNH3 in the 1930s has been optimized down to about 26 GJ/tNH3.

The hydrogen feedstock is generally derived from methane using steam reforming over a Nickel catalyst to produce hydrogen with carbon dioxide as a waste product. Ammonia produced from methane or from hydrogen created from fossil fuelled electrolysis is known as “brown” ammonia if the resulting CO_2 is sent to atmosphere and “blue” ammonia if the CO_2 is captured and stored.

More recently, greener ways of producing hydrogen are becoming more widespread such as electrolysis of water using solar or wind power, but this is less prevalent and, for the moment, less competitive than the steam reforming process, but with the increasing wholesale cost of natural gas, the use of green ammonia is becoming a more realistic proposition.

Ammonia is used extensively in several industries. It is used either as a stabilizer, neutralizer or as a source of nitrogen that can be easily liberated. In countries such as America, anhydrous ammonia is injected directly into the soil as a means of introducing nitrogen into the soil. Nustar Energy’s ammonia pipeline system in the US runs for around 2,000 miles, and transports 1.5 million tonnes of liquid anhydrous ammonia per year from Louisiana and other various points to the “Corn Belt” region to agricultural and industrial customers to the North. 90% of ammonia produced worldwide is used either directly in agriculture or as a feedstock for fertilisers.

Ammonia's alkaline products make it a good ingredient for many household cleaning products. It is also used as a feedstock for chemical products such as nitric acid, dyes, ammonium carbonate, urea, amino acids, phenol, explosives, pharmaceuticals and hydrogen cyanide.

Disassociated ammonia is used in metal treatment operations, such as carbo nitriding, furnace brazing, sintering and bright annealing.

Ammonia in the new "Green Economy"

Producing ammonia from fossil fuels consumes 1.8% of global energy output, emitting 500 MTPA CO_2 (1.8% of global CO_2 emissions).

If the power used in electrolysis of water to produce the hydrogen feedstock is from green sources such as solar or wind turbines, the ammonia created can be truly classed as "green", as the main combustion products of ammonia in air are only nitrogen and water.

Green ammonia (NH3) could play a major role in the decarbonisation of large sectors of the global economy, especially as the natural gas needed to produce brown or blue ammonia becomes more scarce and expensive. There is great potential for decarbonising long-duration energy storage, regional energy and hydrogen transport, shipping and aviation propulsion fuel, and replacing existing brown or blue ammonia production for fertiliser and other chemicals as production of ammonia is more scalable and geographically independent than hydrogen storage, which requires underground salt or rock cavern storage to be scaled up to useful energy storage, which could then be used when or where other green energy is not available.

Ammonia also has a much higher latent heat of vaporisation than hydrogen, resulting in a lower boil-off rate than hydrogen, hence smaller compressor capacity is required for bulk storage.

Plants and bacteria have been producing ammonia for millions of years at mild conditions. This natural method of nitrogen fixation has prompted several research groups to explore the electrochemical synthesis of ammonia at lower temperatures and pressures. Oxford University research has focussed on using photocatalysts to turn sunshine, water, and air directly into ammonia.

In April 2018, the Ammonia Manufacturing Pilot Plant for Renewable Energy started up at the Fukushima Renewable Energy Institute – AIST (FREA) in Japan. The UK's Rutherford Appleton Laboratory, in a £1,500,000 collaboration with Siemens, STFC and the Universities of Oxford and Cardiff, commissioned the world's first "round trip green ammonia pilot plant in 2018. This will allow research to focus on greening the Haber-Bosch process and optimising the process with novel catalysts that allow lower temperature and pressure operating conditions.

Green ammonia appears to be the best choice of fuel for long distance shipping, based on heating value, energy density and storage costs. Although the technology is not new, the challenge will be in the transition away from fossil fuels but companies such as Maersk are driving this transmission..

Green ammonia also has the potential to be a "clean" feed for production of hydrogen gas fuelling aviation. Reaction Engines is working on systems to adapt existing planes to run with zero emissions using ammonia as fuel instead of kerosene. Green ammonia will be stored in the wings and converted to hydrogen using a fuel cell inside the aeroplane. Reaction Engines is also working on systems to adapt existing planes to run with zero emissions using ammonia as a fuel instead of kerosene. To power the engines, ammonia would need to be split into hydrogen and nitrogen using a heat exchanger and a catalyst. The chemical mix would then be ignited in the combustion chamber to create power. The only emissions would be harmless water vapor, nitrogen, and possibly nitrogen oxides, which can be removed using more ammonia. Ammonia does have a lower energy density, which would mean aircraft would have a slightly shorter range.

This will lead to an increase in the need for cryogenic anhydrous ammonia bulk storage tanks at new locations such as ports and airports and this is reflected by the increase in ammonia storage, import and export terminal inquiries received by TGE.

Basic properties of ammonia

Anhydrous ammonia is gaseous at atmospheric conditions. It has the following physical properties

Boiling point:	-33^{o}C.
Vapour pressure:	9 barg at 25^{o}C.
Liquid density:	671 kg/m^3
Latent heat of vaporisation:	1369 KJ/kg

Ammonia vapour is lighter than air, but it vigorously reacts with water vapour to become heavier than air and corrosive (alkaline)

Storage hazards

Flammability and explosivity

Autoignition temperature is 651ºC

Ammonia's flammability range is 16% to 25%. This is a narrow range for combustion, which means that in unconfined areas combustion is unsustainable. Ammonia also has a high minimum ignition energy (380 – 680 mJ) which is two orders of magnitude above the ignition energy of hydrocarbons such as methane and means that it is difficult, but not impossible to ignite. When ammonia does burn, it burns with a low flame temperature (1800 ºC) and a slow flame speed. This leads to deflagration explosion hazards when under pressure or in confined spaces.

Toxicity

Toxic effects of ammonia depend on the amount to which you are exposed (dose), the way you are exposed, the duration of exposure, the form of the chemical and if you were exposed to any other chemicals.

Exposure to low levels of ammonia may cause irritation to the eyes, nose and throat. High levels of ammonia may cause burns and swelling in the airways, lung damage and can be fatal.

Ingestion of ammonia solutions can cause pain and burns throughout the digestive tract. In severe cases the respiratory system, stomach and heart may be damaged and could lead to fatality.

Strong ammonia solutions may cause serious burns if splashed on the skin. At high concentrations, gases and fumes of ammonia can also cause corrosive damage to the skin. Splashes in the eye may cause damage which may be irreversible in some cases and can lead to loss of sight.

The health effects of ammonia are usually immediate and long term effects would not be expected after exposure to small amounts. Presence of ammonia can be detected by most humans, sensing a strong pungent odour at a concentration of around 5ppm.

The concentration that is deemed by NIOSH to be immediately dangerous to life and health (ILDH) of Ammonia is 300 ppm.

The Short Term Exposure Limit for workers over a period of 15 minutes (STEL) is 35 ppm

Solubility in water

Anhydrous ammonia is so hydroscopic that one volume of water will dissolve 1300 volumes of ammonia vapor making water the primary weapon for first responders to reduce the extent of a vapour cloud. When ammonia reacts with water the base ammonium hydroxide (NH4OH) will form.

Environmental

Ammonia is not a greenhouse gas. However, following insertion into crop fields it may be converted to nitrous oxide, an important contributor to radiative forcing of climate. It also has a substantial indirect impact on climate through its role in particulate matter.

Ammonium hydroxide is very alkaline and corrosive so must be kept away from water courses or there will be extensive damage to aquatic life. Allowance should be made for collection and safe removal of the resulting solution from the site.

Stress Corrosion Cracking

This is an issue with low temperature storage and transfer of cryogenic liquids such as ammonia that was first discovered in the 1950s and became identifiable and quantifiable with new inspection technologies introduced in the 1970s. It was also found that initiation of SCC is more difficult and its propagation slower at -33 ºC than at ambient temperatures and is less affected by the oxygen content at the lower temperature.

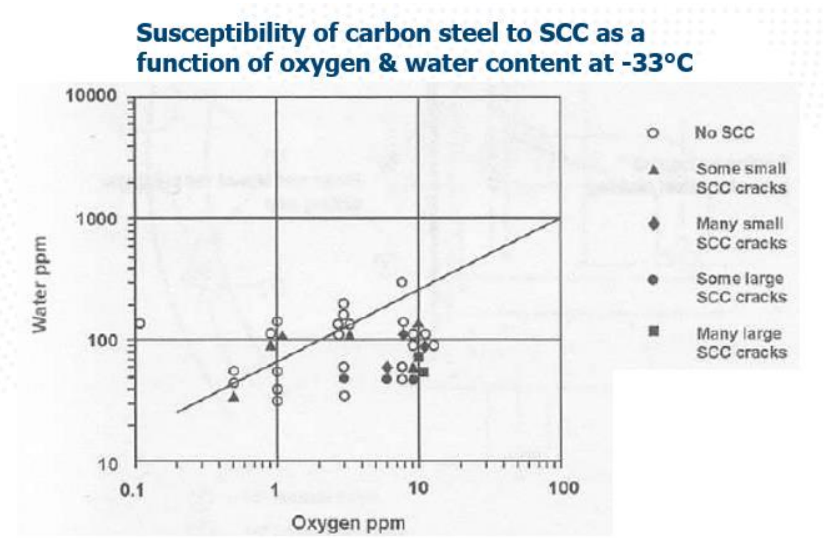

Figure 1. Effect of water content and oxygen content has on stress corrosion cracking in ammonia bulk storage tanks

It can be seen from Figure 1 that in order to further prevent SCC, it is essential that the anhydrous ammonia contains a small amount of water (1000 - 2000 ppm) and that the tank is constantly oxygen free to a value of 0.01% oxygen – lower than normal purging levels in the hydrocarbon storage industry. Nitrogen purging prior to filling is industry standard.

Risk based internal inspection of storage tanks is recommended based on the likelihood of SCC. If SCC is found, it can often be repaired.

Electrical Conductivity

Pure anhydrous ammonia is non-conductive as it has a high dielectric constant. However, with the added water to prevent stress corrosion cracking the liquid becomes conductive. This has meant that conventional in-tank pumps as used in LNG and LPG storage cannot be used as they rely on the product to cool and directly lubricate the pump motor.

Development of safe bulk storage of anhydrous ammonia

Over the last fifty years the design of storage tanks has developed to include principles of inherently safer design, thus reducing the risk of major accidents to a level that is reasonably practicable (ALARP).

Single containment - Pressurised sphere or "bullets"

Up until the 1970s, anhydrous ammonia was generally stored in pressurised vessels, such as spheres, or in long cylindrical pressure vessels with dished ends, sometimes referred to as "bullets". Storage was at atmospheric temperature at pressures of around 15 barg.

These single containment vessels were built to pressure vessel codes but were susceptible to external fires. If the vessel fails catastrophically, a large expanding toxic vapour cloud is created from the boiling liquid, covering a large area.

Another issue with storage in spheres was Stress Corrosion Cracking, . Widespread SCC in liquid ammonia storage spheres. For this reason, many of the facilities which stored ammonia in the fully-pressurised or semi-refrigerated form were decommissioned and were replaced by fully-refrigerated storage systems

Single containment - Refrigerated atmospheric cryogenic storage

LNG was stored at atmospheric pressure and a temperature of -33 ^{o}C in a low temperature carbon steel tank. The tank was placed on loas bearing base insulation placed on a reinforced concrete slab and externally insulated on the shell and roof to keep the product cold. In case of spill protection, a remote earth bund was provided around the tank, which would prevent the wider spread of spilled liquid ammonia but would not stop large toxic gas clouds from being produced and ammonia would seep into the ground, damaging the local environment.

Filling was usually via a roof connection and the outlet was near the bottom of the tank. Electrical heating of the base was required to prevent "frost heave" of the ground beneath the tank

As the toxic consequences of a loss of containment are so high, many of the original single containment ammonia tanks have been re-fitted to provide secondary containment.

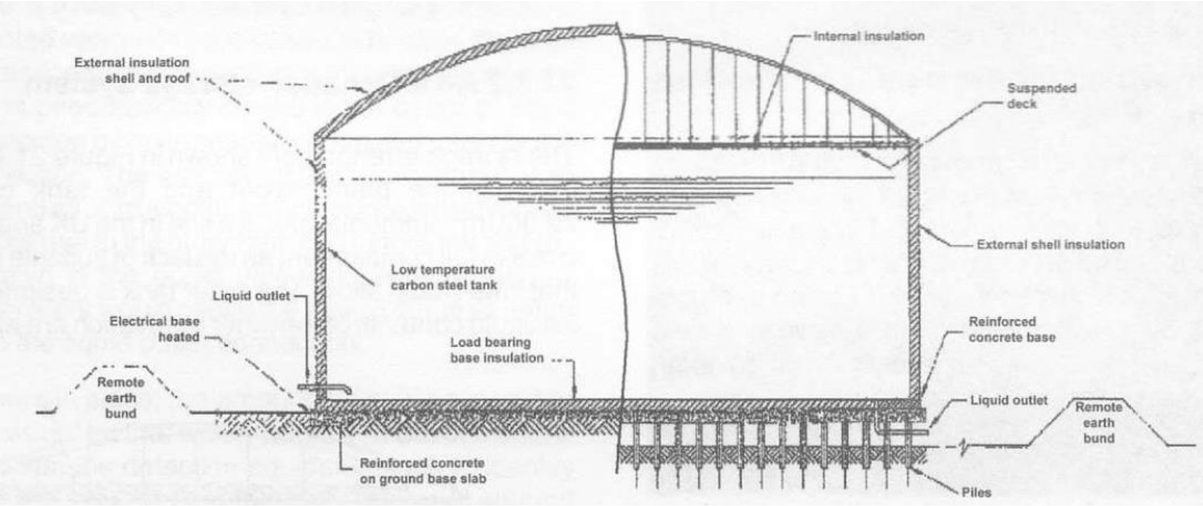

Figure 2. Typical arrangement of a single containment cryogenic ammonia bulk storage tank

Double Containment

The inner tank is designed to store the liquid ammonia at -33 °C under normal conditions and is again made from low temperature carbon steel. The outer tank is normally empty or filled with insulating material such as perlite, but must also be capable of containing either a liquid leak or overflow from the inner tank. The outer tank is not designed to contain vapour from an ammonia leak so a failure of the inner tank will release vapour to the atmosphere. The tank is placed on an elevated piled suspended deck in order to prevent ground heave.

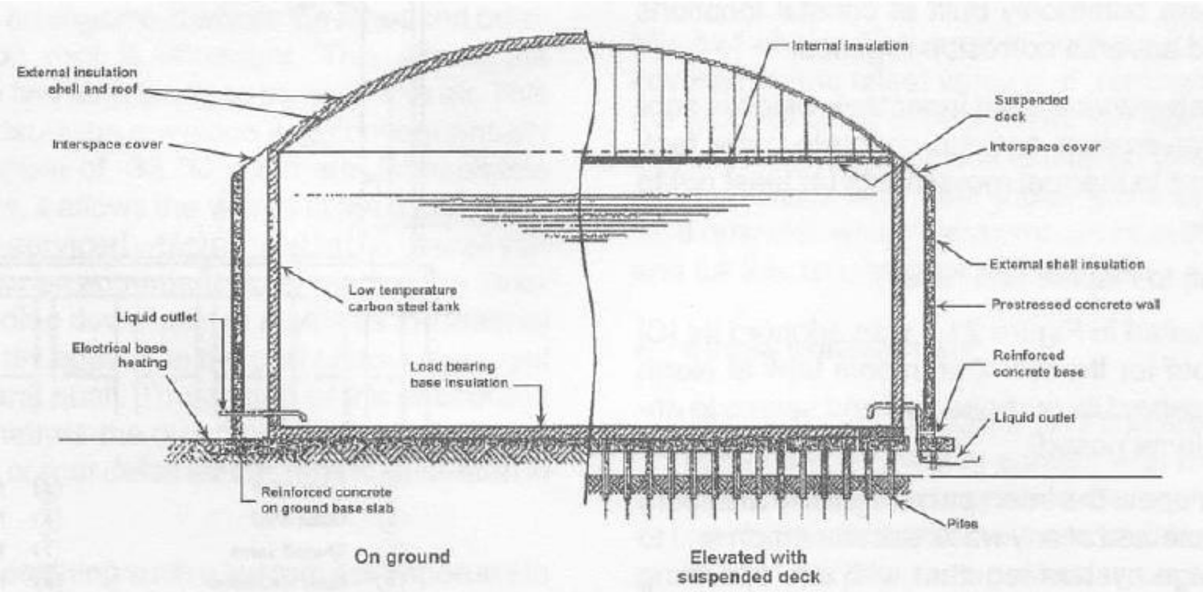

Figure 3. Typical arrangement of a double containment cryogenic ammonia bulk storage tank

“Full” Containment

This consists of an integrated refrigerated low temperature carbon steel internal tank inside a vapour-tight outer tank, which may be made of low temperature carbon steel or reinforced or post-tensioned concrete. Tanks often have a bottom outlet to a send-out system but with actuated emergency shutdown valves between the tanks to isolate the tank in case of a loss of containment downstream of the tank. If the inner tank wall fails, the contents are fully contained within the outer tank, so there is no need for an external bund. The outer tank is also designed to contain the ammonia vapour. The inner tank has a suspended roof

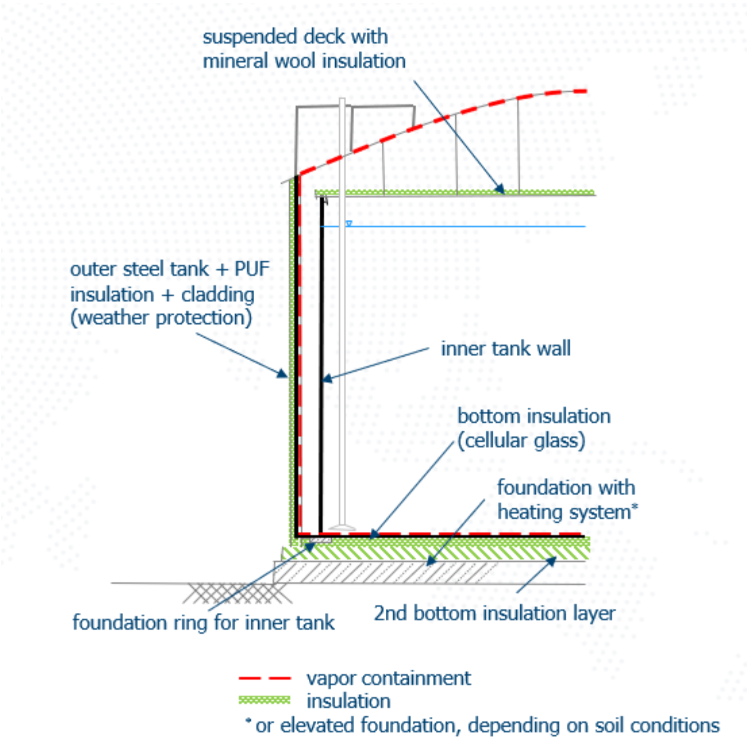

Figure 4. Typical arrangement of a full containment cryogenic ammonia bulk storage tank

It can take up to a month to purge a tank for entry and internal inspection. With a steel/steel design it is much easier to purge the tank and remove trace ammonia from the annulus which is much more difficult if the annulus is filled with insulating material.

Recent technology developments have led to the introduction of roof-mounted In-Tank Pumps that are suitable for ammonia, which greatly reduce the possibility of a large loss of containment during send-out, as the pump can be isolated . These pumps are mounted at the bottom of columns containing a nitrogen-purged motor enclosure and electrical containment system, where the electric motor housed in a liquid and gas tight enclosure and is indirectly cooled by the product liquid. There is a filtered product liquid bearing and coupling lubrication system. The motor is magnetically coupled to the pump. The power cable assembly enclosed in a flexible bellows type hose assembly,

A foot valve allows the column to be purged with nitrogen allowing maintenance or replacement.

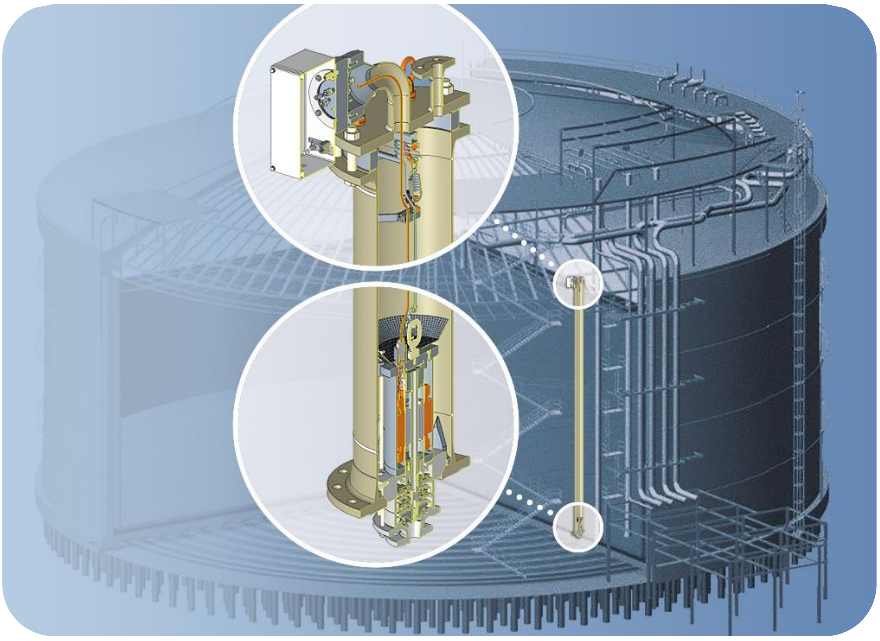

Figure 5. Typical arrangement of a full containment cryogenic ammonia bulk storage tank

Ammonia Storage Terminal Design

A typical modern ammonia storge terminal shown below.

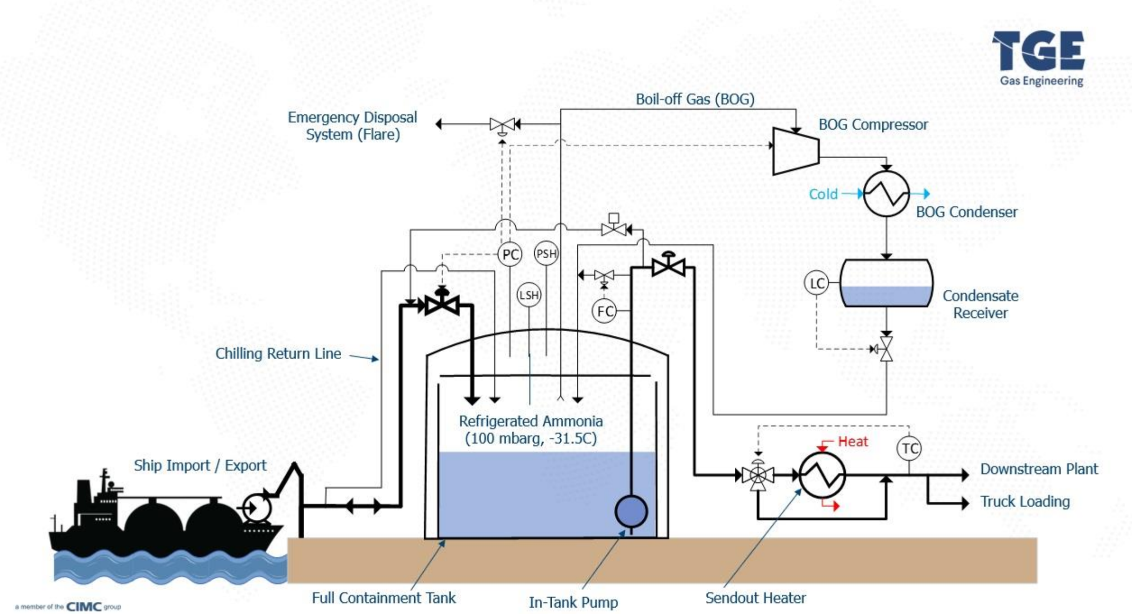

Figure 6. Typical design for an ammonia storage terminal

Loading arms at the jetty are connected to ships which can then pump their cargo into the storage tank. The transfer line is pre-chilled using ammonia pumped from the tank to prevent vaporisation in the line. In-tank pumps can send out ammonia to downstream process users, or to truck loading facilities for export by road or rail via a heat exchanger export to allow for pressurised transport at atmospheric temperature. Loading to refrigerated ships is also possible via the unloading line. Boil-off gas is compressed and returned to the tank. If compression is unavailable, boil off gas will be sent to an emergency disposal system such as flare or scrubber.

Process Safety Design Issues

Modelling releases of anhydrous ammonia vapour

The vapour density relative to air is 0.6, so one would expect a gaseous release of anhydrous ammonia from a tank-top PSV to rise and dissipate in the atmosphere. Modelling with programs such as PHAST and FRED show such outcomes. However, in reality, anhydrous ammonia will associate with any moisture in the air to form a white ammonia hydroxide cloud which is heavier than air and will roll along the ground.

Modelling releases of refrigerated anhydrous ammonia liquid

A large spill of refrigerated liquid anhydrous ammonia will form a pool on the ground which will initially vaporise at a fast rate, taking heat from the ground, but the rate will slow down as the pool freezes the ground. The liberated vapour will take any moisture in the air to form a dense white cloud of ammonium hydroxide, as above,

Requirement for Fire Water

As ammonia will not readily burn, fire protection of the storage tank is only really necessary to provide cooling from the effects of an external fire if other chemicals are present close by. Concrete outer tanks provide good thermal insulation from these effects.

Water reacts violently when sprayed onto pools of ammonia, creating large clouds of toxic ammonium hydroxide and its direct use should be avoided in the event of a loss of containment. . Emergency response needs to focus on preventing the large vapour clouds from a release of ammonia from reaching populated areas inside and outside the facility. Automatic and/or remotely operated water curtains where a water mist is sprayed which will dissolve the vapour and prevent it from reaching populated areas.

Conclusion

Although it has a serious toxicity hazard, anhydrous ammonia can be safely stored in bulk. Best practice is a full containment tank with roof-mounted in-tank pump as this effectively eliminates large loss of containment. Stress corrosion cracking can be avoided by storing the ammonia at low temperature and atmospheric pressure and by maintaining a water content of 0.1 to 0.2% in the anhydrous ammonia. Oxygen should be removed by purging the storage tank with nitrogen before filling.

References

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Long, B ,Garner, B, Guide to Storage Tanks and Equipment, 2003,