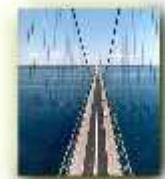


Super-Safe Large Anhydrous Ammonia Tanks

*New Designs for Ammonia Storage Safety
Prevention Design for Populated Environments*

Mackinaw Associates

Super Safe NH₃ Storage Infrastructure



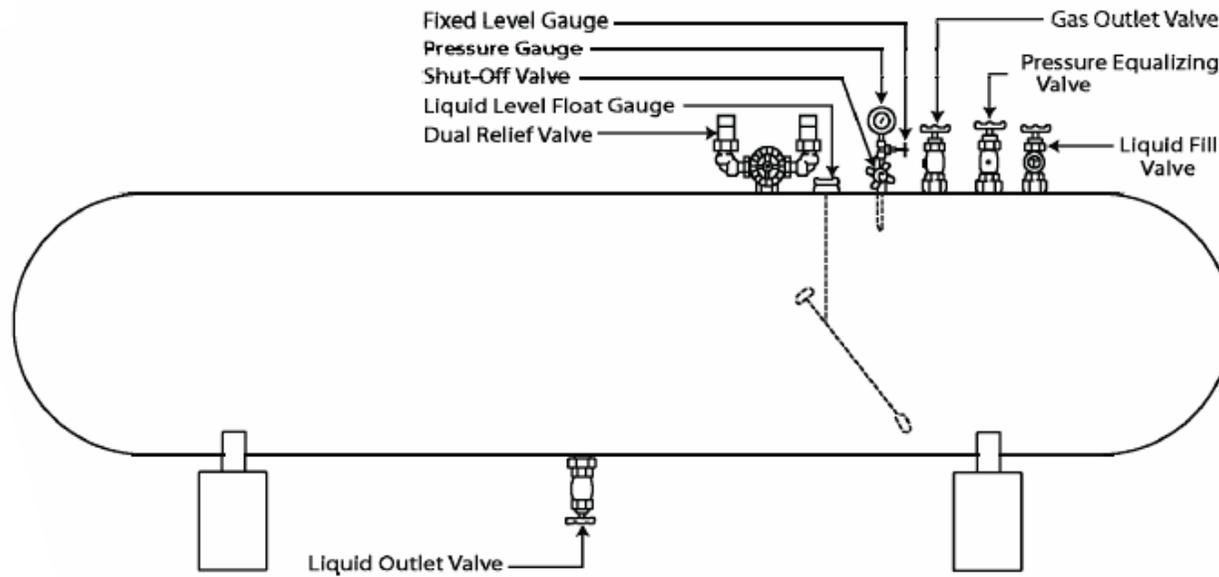
Introduction



- History of hazardous liquid tanks (non-automotive)
- Quick review of how ammonia is stored, large and small
- Safety Record: safety track record for ammonia is good
- Argument: New safer tank designs are needed to insure public safety where large stationary urban tank farms/tanks exist.
- Materials and Regulations – Other industry examples...
- Example - Rail Traffic:
 - Chlorine – 32,150 tank cars per year
 - Anhydrous Ammonia - 40,764 tank cars per year
 - Petroleum Gas - 56,000 tank cars per year (rail) (Jack Aherne - US Transportation Security Administration).



TYPICAL HORIZONTAL ANHYDROUS AMMONIA STORAGE TANK



Ammonia Incident Summaries – *Minnesota Department of Agriculture*

Tractor-Trailer Tip Over in Mankato, Minnesota, October 20, 2005

At approximately 10:20 a.m. on October 20, 2005, a tanker truck hauling 20 tons of anhydrous ammonia rolled over onto its side just off Highway 169 shutting down portions of the highway and causing the evacuation of local residences in Mankato. Although little if any ammonia released the potential existed and therefore as a precaution a limited evacuation was warranted. Since the trailer was on its side, only a limited amount of ammonia could be off-loaded through the valves. Once up-righted the remaining ammonia was pumped out into another tanker.

Mankato Free Press-Online, Mankato, Minnesota. Selected stories from October, 2005.

Nurse Tank Rupture, June 6, 2005

An internal non-code weld had weakened the shell of an anhydrous ammonia nurse tank causing the tank to rupture. The full, pressurized tank was propelled across the facility yard narrowly missing bulk agricultural chemical tanks and buildings as it flew. The tank came to rest approximately 250 feet away after first splitting a tractor in half. An extensive cloud of ammonia vapor drifted away from all major populated areas although some nearby residents were treated for exposure. This tank was manufactured in 1973.

Minot, North Dakota Freight Train Derailment, January 18, 2002

At approximately 1:37 a.m. on January 18, 2002, a freight train derailed 31 of its 112 cars about ½ mile west of the city limits of Minot, ND. Fifteen of those 31 cars that derailed were hauling anhydrous ammonia. A total of 240,000 gallons of anhydrous ammonia released to soil and air creating a vapor plume that covered the derailment site and drifted toward Minot. One resident was fatally injured, 11 people sustained serious injuries, and 322 people, including the two train crew members, were seen by medical personnel. Damages exceeded \$2 million and more than \$8 million has been spent for environmental remediation.

National Transportation Safety Board. 2004. Railroad accident report, NTSB/RAR-04/01.

Anhydrous Ammonia Pumped into Propane Storage Tanks, October 21, 1999

Two 30,000-gallon propane tanks, each at seventy percent capacity were accidentally topped off with anhydrous ammonia. Similar plumbing on both transport and storage tanks made the transfer possible. The galvanized fittings on the propane tanks would have corroded through causing the release of ammonia and propane if not immediately emptied. Compounding the problem was that the individual pressures of ammonia and propane together in a tank are additive which would have caused pressure relief valves to open when the internal tank temperature reaches 70°F.

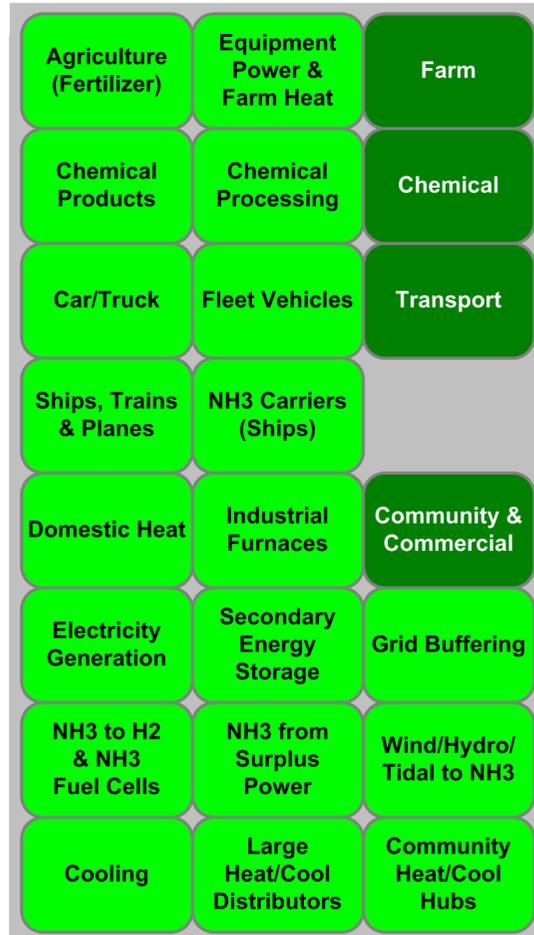
<http://www.mda.state.mn.us/chemicals/spills/ammoniaspills/summaries.htm>



Function Activities



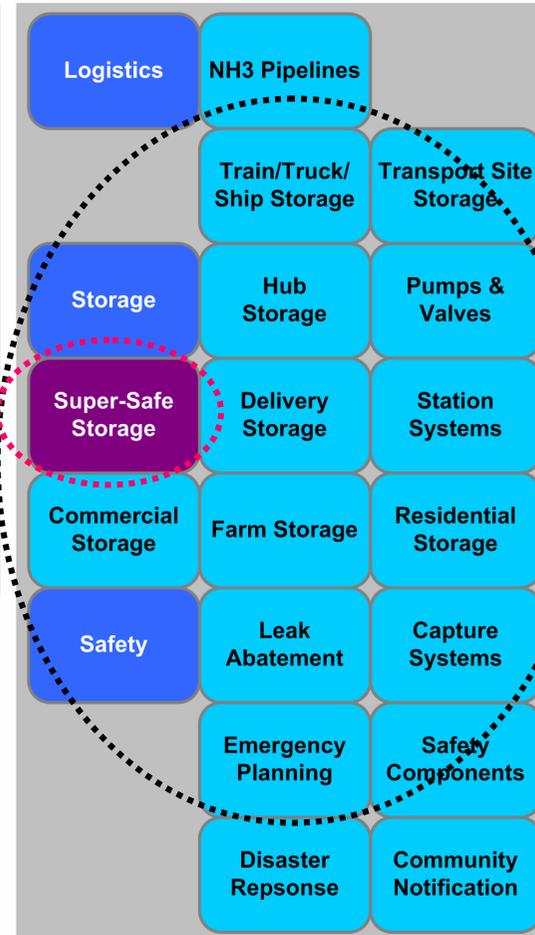
Ammonia Use



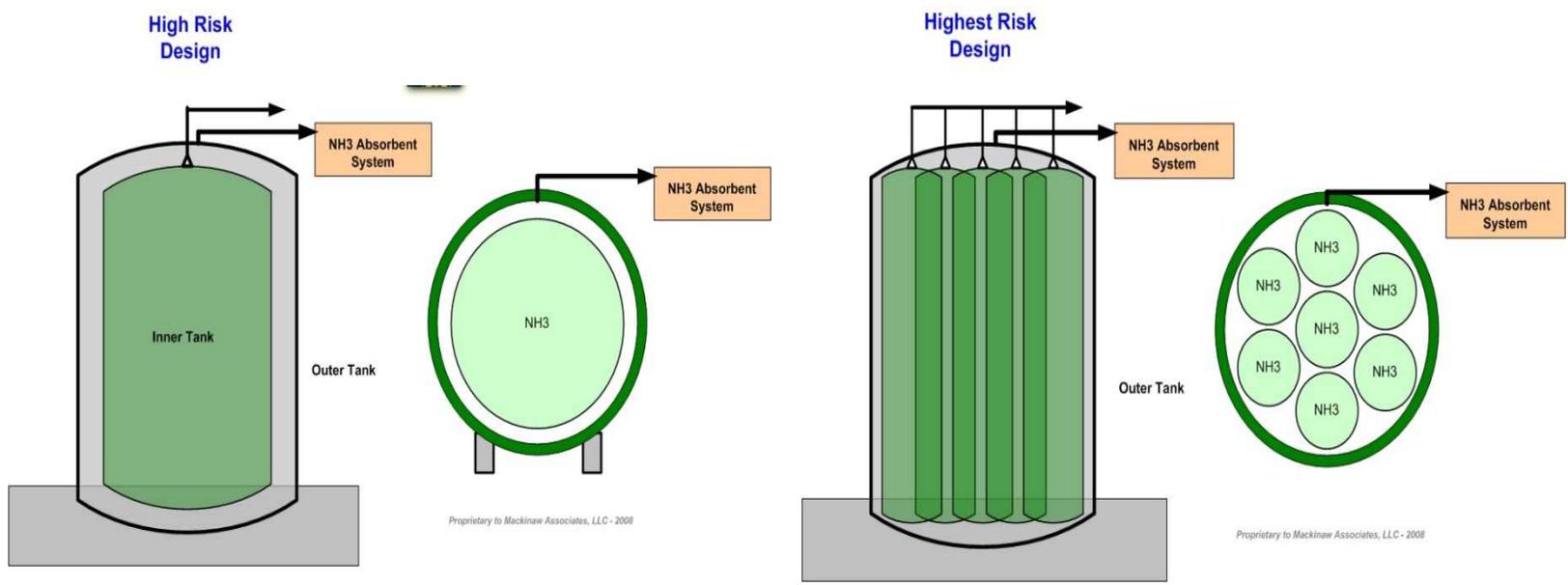
Ammonia Production



Infrastructure

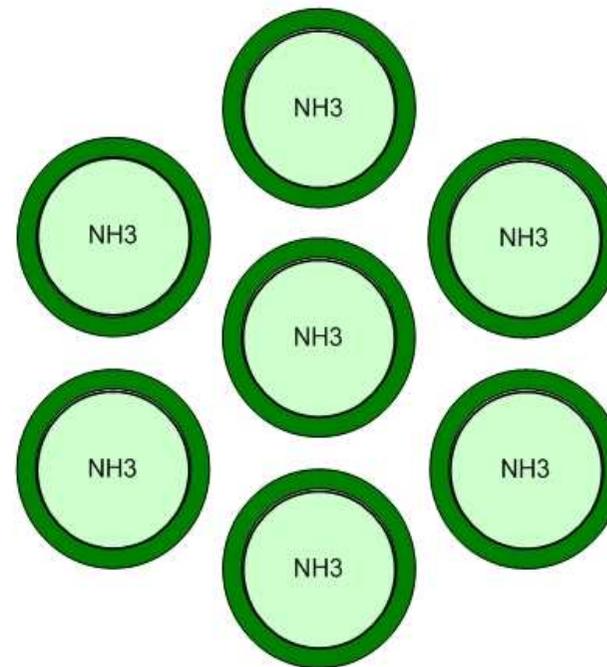
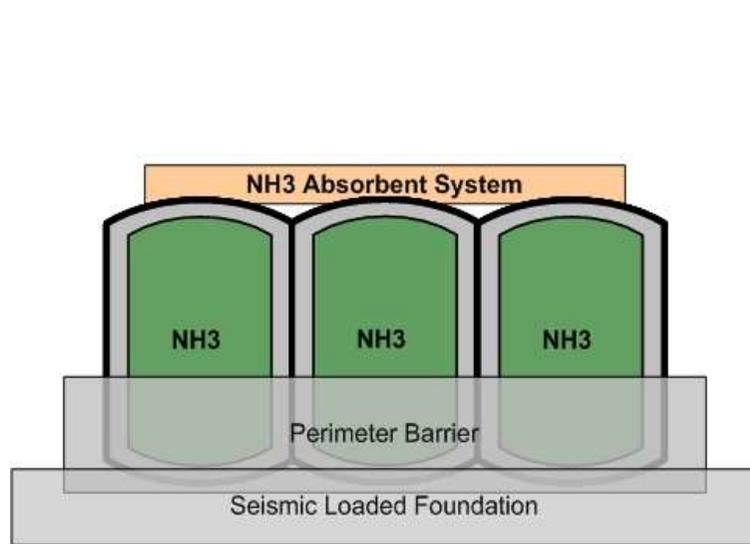


Upright Tank Concepts



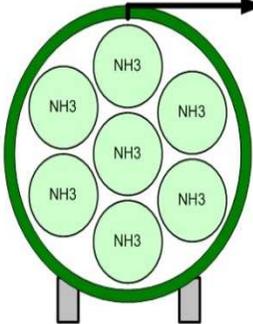
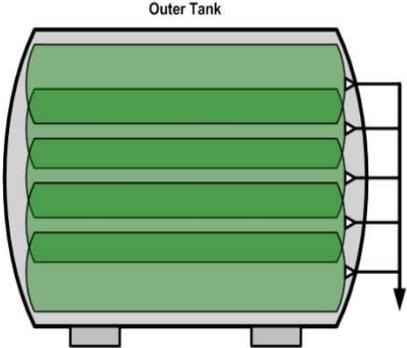
Urban Location - Tank Farm

Tank Farm



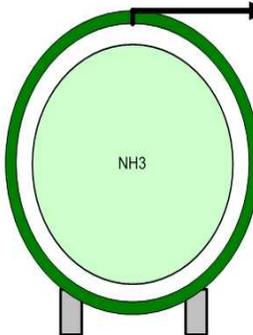
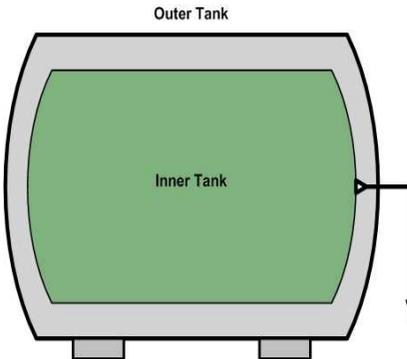
Horizontal Tank Concepts

Highest Risk Design



Proprietary to Mackinaw Associates, LLC - 2008

High Risk Design

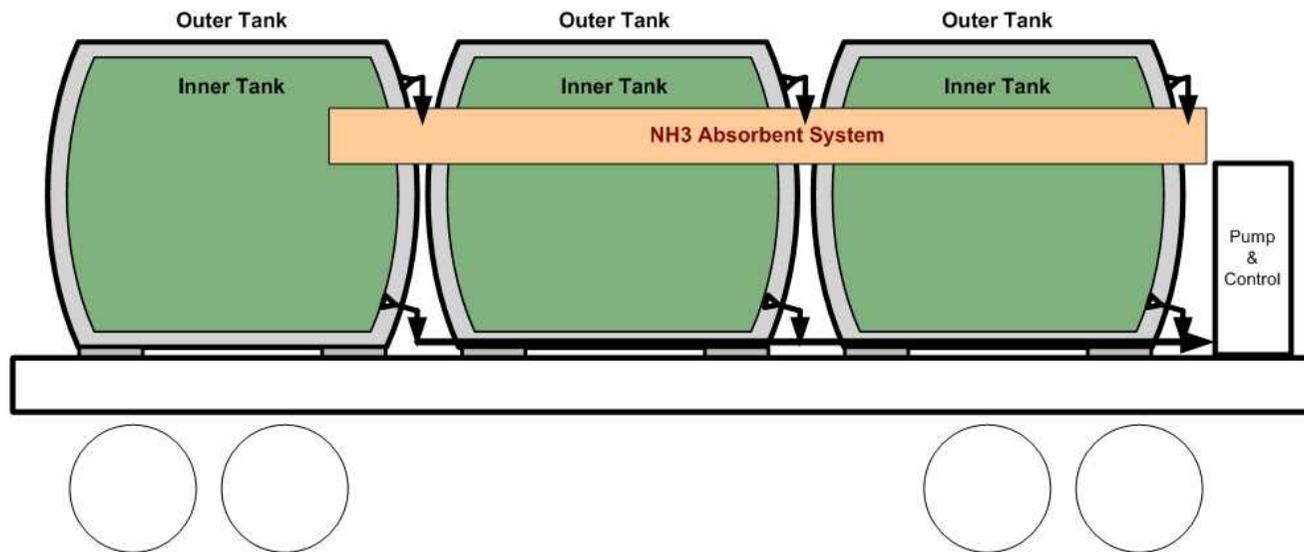


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Multiple Tanks – Transport Application

Transport
Design



Typical current design:
33,800 gallons
Union Tank Car Company



Issues

- Public acceptance of NH₃ fuel could hinge on fail-safe storage and delivery. Perceptions vs. Realities.
- OSHA, Pressure Vessel Certificates, US and Canadian practice guidelines ... other applicable standards and regulations, as well as best practices.
- Difficulties in storage
 - Corrosion
 - Reactions
 - Pressure issues (ambient temperature factors, ammonia venting, ammonia transfer issues, breakaway valves)
- What is involved with super-safe storage
 - tanks, fittings/valves, hoses, sensors,
 - active neutralization

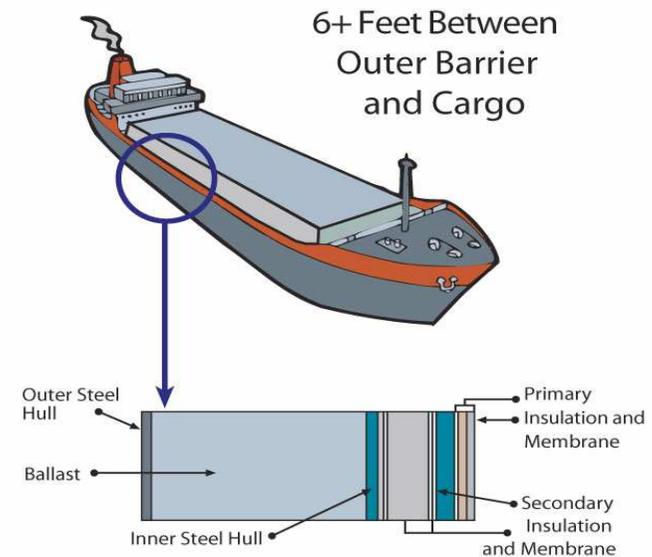


More

- Large and small super safe concept designs
 - Smaller tanks vs. huge tanks ... if something goes wrong fewer are effected (limit capacities of tanks stationed near communities)
 - Double hulled (tanks-with-a-tank or tank within a tank)
 - Neutralization of vented ammonia - designs to capture vented NH₃ and to neutralize same using automated method - sensors alert system)
- Relative cost and availability
 - Steel & others materials (aluminum, composite, fiberglass, etc.)
 - What adds costs vs. what safety and insurance considerations may be



The Safety Math



- A very good history to date – yet some policies will demand some new designs
- Ammonia vs. Propane, Gasoline, Hydrogen, etc.
- Multiple Tanks vs. Monolithic Tank designs
- Double-Hull vs. Single-Tank
- Capture & Neutralization Systems
- Connection Systems Safety
- Seismic, Puncture, and Placement precautions
- Alerts & Monitoring
- Training & Education



Conclusion

Futures

- What is needed - what should be envisioned.
- Public relations and compliance
- What is already understood
- Predicting policy need & technology responses
- Certification – fabrication & systems
- Which way will public perception go?



Questions?

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NOTES - History of hazardous liquid tanks (non-automotive)

To understand the dynamics and challenges related to Ammonia storage I believe it is important to understand the history of hazardous liquid storage in the US. Storing hazardous liquids has changed considerably since wooden barrels were used to store oil in the late 1800. As time passed they were replaced by riveted steel tanks and eventually, welded steel storage tanks.

Codes to regulate hazardous liquids and standards for performance testing and construction of storage tanks were developed in the first half of this century, and continue to be refined.

In the 1960 and 70s concern for lost inventory was the driving force behind construction and safety standards. Between the 1970s and 1990s environmental concerns started to drive technological advances for the safe storage of hazardous liquids.

In more recent times, environmental awareness, public safety, media attention and public concern has forced us to consider more stringent storage requirements. In the early 1900s an association of steel tank manufacturers -- which later would become Steel Tank Institute (STI) -- was formed. Around the same time, a third-party testing laboratory -- Underwriters Laboratories (UL) -- was developing its first safety standards for atmospheric steel storage tanks.

The National Board of Fire Underwriters published NBFU 30, today that standard is known as NFPA 30 (Flammable and Combustible Liquids Code). Many governmental bodies in the U.S. today reference the NFPA standard either by legislation, statutes or ordinances to give local or regional officials an enforceable code document. The NFPA code cites various construction standards written by UL, STI, and ASME among other groups, as acceptable construction practices and standards.

In the 1920s and 30s welding replaced riveting for most steel tank construction leading to higher quality tanks. The '60s tank buyers hoped to avoid the inevitable problem of steel underground storage tanks releasing product due to corrosion. At that time, environmental concerns did not drive new product development. Foremost on the mind of tank owners were inventory conservation and the cost to replace lost product. Corrosion was controlled through paint, synthetic linings and coating, and cathodic protection.

Leaking underground tanks became an issue in the 1970s and improved construction, inspection and monitoring requirements were implemented. In the 1980 a growing number of customers were searching for enhanced environmental protection and dual-walled tanks were developed. A dual-walled tank consists of an outer wall of steel intimately wrapped over the primary tank. The external wall can be a thinner gauge of steel. Due to the intimate wrap, the two walls act as a single structural unit, reducing the costs to build the tank.

By 1982 many local, state and county officials were addressing the growing problem of leaking underground storage tanks through enactment of regulations. In 1984, the U.S. Congress approved a law to regulate underground storage tanks. By that time, media attention was reaching a peak, and

Congressional action led to development of a federal regulatory program. The federal government's technical requirements called for corrosion protection for tanks and piping, structural integrity, release detection, proper installation, corrective action and secondary containment for the storage and handling of hazardous materials.

The U.S. regulatory program spurred significant changes in the tank industry and unveiled a completely new trend -- a demand for aboveground storage tanks. Because of the negative headlines associated with expensive cleanups -- including contaminated soils and water resources -- tank owners began to think seriously about the advantages and disadvantages of owning an underground tank system. Many elected to close their tanks.

With the suddenly strong demand for aboveground tanks, the codes needed to find a way to allow the safe siting of aboveground tanks and major provisions were added to codes in the early 1990s. The Environmental Protection Agency proposed revisions to their Spill Prevention Control and Countermeasure, SPCC, The first revision to the SPCC rule proposed in 1991 was to require secondary containment that was impermeable for at least 72 hours after a release occurred. The initial tank industry solution was to install a single wall aboveground tank into a steel dike.

Tank owners quickly realized that a double-wall steel aboveground tank, similar in construction to the double-wall steel underground tank, could fulfill the same function as a diked tank. Soon, the double-wall aboveground tank became available in both horizontal and vertical construction as a popular installation option. The trend towards secondary containment makes perfect sense. It provides containment to prevent releases to the atmosphere, into the soil, groundwater, or surface waters and all the undesirable elements that go with a release -- report writing, cleanup, lawsuits, business interruptions, and potential regulatory enforcement acts. It provides an extra insurance policy, just in case the tank was improperly installed or maintained. It offers peace of mind to the tank owner.



How ammonia is stored, large and small

Anhydrous Ammonia Storage

Tank Truck - 11,500 gal @ 300 psi

Rail Car - 33,500 gal @ 340 psi

Pressurized Stationary Tank - 2000 – 120,000 gal @ 250 psi

Producing Plant & Large Distribution Terminals Refrigerated Storage ~ 30,000 tons @ < -28 °F, 15 psi

Existing Ammonia Rail Car Fleet

- Number of Cars in Service: ~ 6000
- Average Age of Fleet (est.): 25 years
- Maximum Allowable Service Life: 40 years

Ammonia storage facilities

Liquefied ammonia is stored either at ambient temperature under high pressure or at -33°C under atmospheric pressure.

Tanks come in many shapes and forms. Large tanks are erected in the field. Smaller tanks are produced in a factory and shipped to the site for installation.

Shop-built tanks are made for underground installations and for aboveground installations. Aboveground tanks are either oriented for horizontal or vertical installation, and are produced in a cylindrical form. The tanks are capable of being designed and fabricated as pressure vessels, or vented to atmosphere. The tank can have compartments internal to the tank. Tanks are often secondarily contained. The tank can be insulated for fire safety or temperature control. Corrosion protection can be given to exterior tank bottoms in contact with soil or to the tank interior with special coatings and linings. Some aboveground tanks are even installed in an underground vault or room.

Shop-fabricated aboveground tank construction.

A shop-fabricated tank is typically 50,000 gallons capacity or less. That capacity translates to a 12' diameter by 60' long tank, just small enough to fit on a transport truck and be shipped on a highway. Any truckload wider than 8.5' requires a permit and any truckload over 12 in width requires a special highway escort. Bridge underpass limitations, weight restrictions, and tank trailer length capabilities further restrict highway transportation shipments, such that tanks larger than 50,000 gallons are more economically erected in the field, rather than at the shop.

Atmospheric tanks

The main types of atmospheric tanks operating at -33°C are:

A. Single wall tanks, which are tanks with one steel bottom and wall designed to contain the full liquid level of ammonia.

B. Double wall tanks, which are tanks with double steel bottom and wall, each designed to contain the full liquid level of ammonia.

To better understand the differences between single and double wall, and the meaning of full containment, one or more of the following barriers can be considered:

1. Inner steel tank designed for full containment of liquid ammonia.
2. Outer steel tank designed for full containment of liquid ammonia, the roof may be separate for each inner and outer tank or common.
3. Concrete or steel wall designed as extra tank protection, not designed for containing liquid ammonia.
4. Bund wall (or dike) with height and distance designed to contain liquid ammonia that may be released from the ammonia tank in an accidental situation. Examples of different constructions of bund walls are shown.

Pressurized Anhydrous Ammonia Storage Tanks (Stationary)

Anhydrous ammonia storage tanks are of the above ground, carbon steel, horizontal type, stress relieved with spherical heads, ranging in capacity from 1,000 to 50,000 water gallon.

Each tank is built in accordance with the latest edition of the ASME Code for Unfired Pressure Vessels, Section VIII, Division 1, rated for 250 to 300 psi and are registered with National Board.



Safety Record: safety track record for ammonia is good 2003

Chemical	#Incidents	Fatalities	Rel. Freq.
Gasoline	3936	82	5.3x
LPG	915	9	2.5x
Anhydrous Ammonia	1016	4	--

The tanks themselves are rarely the problem. It's the valves and fittings, and human error in transfer to/from the tank. Eliminate all human contact with the storage and delivery system. Lots of redundant sensors and controls.

Argument: New safer tank designs are needed to insure public safety where large stationary urban tank farms/tanks exist.

Many of the energy storage concepts we discussed yesterday would require ammonia to be stored and transported near and in urban areas.

Any significant release near urban areas could have disastrous effects not only for the population but for the public image of ammonia as well.

But just as important small release that are not significantly hazardous noticed by the populace will have a major impact on public acceptance of ammonia in our daily lives.

Materials and Regulations – Other industry examples...

Example Concern - Rail Traffic:

Chlorine – 32,150 tank cars per year

Anhydrous Ammonia - 40,764 tank cars per year

Petroleum Gas - 56,000 tank cars per year (rail) (Jack Aherne - US Transportation Security Administration).

Significant amounts of various hazardous materials are transported throughout this country without significant incident.

But we should not be content with our track record and learn from other industries such as nuclear power where an

At 4:00 a.m. on March 28, 1979 Three Mile Island Unit 2 changed the viability of that industry for ever in the United States.

Typical Pressurized storage tank

Talk about exposed valves

Ammonia Incident Summary

Incidents of ammonia spills- mostly human failures

Function Activities- Ammonia-centric

This is a chart cover function and applications of ammonia; we are concentrating on infrastructure and super safe storage.

Tank Examples- Upright, Urban, Horizontal, Transportation

Public acceptance of NH3 fuel could hinge on fail-safe storage and delivery. Perceptions vs. Realities.

Any significant release near urban areas could have disastrous effects not only for the population but for the public image of ammonia as well.

But just as important small release that are not significantly hazardous noticed by the populace will have a major impact on public acceptance of ammonia in our daily lives.

DOT's tank cars

Railroad tank cars used to transport hazardous materials have a shell puncture-resistance system capable of withstanding impact at 25 mph and a tank-head puncture-resistance system capable of withstanding impact at 30 mph.

The rupture of tank cars and loss of lading are principally associated with the car-to-car impacts that occur as a result of derailments and train-to-train collisions.

Conditions during an accident can be of such force that a coupler of one car impacts the head or the shell of a tank car. With sufficient speed, such impacts can lead to rupture and loss of lading.



OSHA, Pressure Vessel Certificates, US and Canadian practice guidelines ... other applicable standards and regulations, as well as best practices.

NFPA, ASTM, DOT, OSHA, STI (Steel Tank Institute), *Vessel Certificates*,

Materials – Regulations

1. The American national standard safety requirements for the storage and handling of anhydrous ammonia "K61.1 -1989".
2. The current edition of the American society of mechanical engineers boiler and pressure vessel code, section II; section V; section VIII, division 1; and section IX.
3. The current edition of the national board inspection code, an American national standard.
4. The American society for nondestructive testing standard "SNT-TC-1A".
5. The current edition of ASME B31.3, the American national standard for chemical plant and petroleum refinery piping.
6. The current edition of ASME B31.5, the American national standard for refrigeration piping.
7. The American petroleum institute standard 620, recommended rules for design and construction of large, welded, low-pressure storage tanks.

Minimum requirements for new storage containers other than refrigerated storage containers

- a. American society of mechanical engineers constructed and so stamped;
- b. National board registered;
- c. Metal specified tensile strength not exceeding seventy thousand pounds per square inch [482636 kilopascals]; ASTM 516 gr. 70
Carbon 0.27 - 0.31%
Manganese 0.79 - 1.3%
Phosphorous 0.035% max
Sulphur 0.035% max
Silicon 0.13 - 0.45%
- d. Head and shell materials for storage containers made in accordance with fine grain practice;
- e. All welds post-weld heat treated after construction, for all storage containers ordered or installed after January 1, 1996. A storage container does not require post-weld heat treatment if the implement is fabricated with hot formed heads or with cold formed heads that have been stress relieved; and (excessive stress can cause brittle fracture)
- f. Storage containers exceeding six thousand water gallons [22712.4 liters] in capacity must be equipped with a manhole opening.
- g. Pipe and pipe fittings must not be cast iron, brass, copper, zinc, or galvanized.



Difficulties in storage

Corrosion, Reactions, Pressure issues (ambient temperature factors, ammonia venting, ammonia transfer issues, break-away valves).

Ammonia will not corrode iron or steel, but will react rapidly with copper, brass, zinc and many alloys, especially those containing copper. Only steel or ductile iron should be used for ammonia containers, valves, fittings and piping. A storage tank is usually considered to have an 85% usable capacity. (A 15% vapor space must always be maintained when filling, to allow for expansion). Liquid ammonia exerts a vapor pressure which increases with rising temperature. When liquid ammonia is in a closed container, it is in equilibrium with ammonia vapor and the pressure within the container bears a definite relationship to the temperature.

What is involved with super-safe storage?

Double walled tanks, breakaway fittings/valves- packing valves and delivery lines with active neutralization (Dry citric acid), hoses, ammonia sensors alert systems, active neutralization (Dry citric acid). Capture of spills/releases inside double walled tanks for contained recovery. Evacuation of contaminated tanks through active neutralization (Dry citric acid).

Dry citric acid sprinkled on "live" liquid NH₃ just produced this innocuous dirty-snow-like reaction product. Stopped the NH₃ dead in its tracks and there was essentially zero vapor pressure of NH₃ from the product. Neutralize liquid anhydrous ammonia (puddle of standing NH₃, no water) by spreading dry citric acid (C₆H₈O₇) powder over the puddle. The reaction product looked like dirty snow, and had virtually zero ammonia odor.

Large and small super safe concept designs

Smaller tanks vs. huge tanks ... if something goes wrong fewer are effected (limit capacities of tanks stationed near communities)

Double hulled tanks-with-a-tank or tank within a tank.

Neutralization of vented ammonia - designs to capture vented NH₃ and to neutralize same using automated method - sensors alert system) Dry citric acid sprinkled on "live" liquid NH₃ just produced this innocuous dirty-snow-like reaction product. Stopped the NH₃ dead in its tracks and there was essentially zero vapor pressure of NH₃ from the product.

Relative cost and availability

Steel and others materials (aluminum, composite, fiberglass, etc.) What adds costs vs. what safety and insurance considerations may be

Steel is still the most cost effective material for large tanks. Understanding the various standards and using appropriate levels of labor, materials and controls directly impacts the cost of manufacture.

Union coded shop vs. Union non-coded shop vs. Non-union, non-coded shop

Non-coded shops can still build in accordance with the pressure vessel code, lower cost.

Futures

What is needed - what should be envisioned?

Public relations and compliance

What is already understood

Certification – fabrication & systems

Which way will the wind blow?

With super safe construction, tank owners now have viable options for the safe storage of ammonia near or in urban areas. Tank owners are now given the choice of an economic, environmentally and politically sound tank installation. A secondary containment tank is a valuable commodity. However, the tank in itself will not ensure full compliance and public acceptance. Serious attention must be given to the entire system, including o the piping system, pumps, valves, and other important aboveground tank system components as well as training, operations and improved emergency response.

