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Ammonia Safety

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Outline

- Is there a Safety Issue?
- Current Level of Safety
- Integrate Safety Into the System
- Look for Inherently Safe Approaches
- Summary and Conclusions

My goal – have you accept two points

"We must accept the inexorably rising standards of technology, and we must relinquish comfortable routines and practices rendered obsolete because then may no longer meet new standards." **Admiral Hyman Richover**

- As the use of ammonia increases, without safety improvements, the frequency if incidents will increase. This comes at a time when we need the acceptance of a wider group of people who will be encounter ammonia more frequently

Yes, there is a Safety Issue

- Whenever a there is a new application of an old technology
  - Perceived risks can be high even when the actual risk is quite small – if I can smell it, it must be doing damage to me. Ammonia can be smelled at concentations at least an order of magnitude below where it poses a hazard
  - Releases with fatalities have occurred during ammonia handling and transport, while there are many more fatalities during gasoline handling and transport, without improvements the frequency of ammonia transport fatalities will increase as the use of ammonia expands
- Ammonia has been handled safely for decades, and we have the technology to lower the safety risk even further
- Continuous improvement should still be a goal

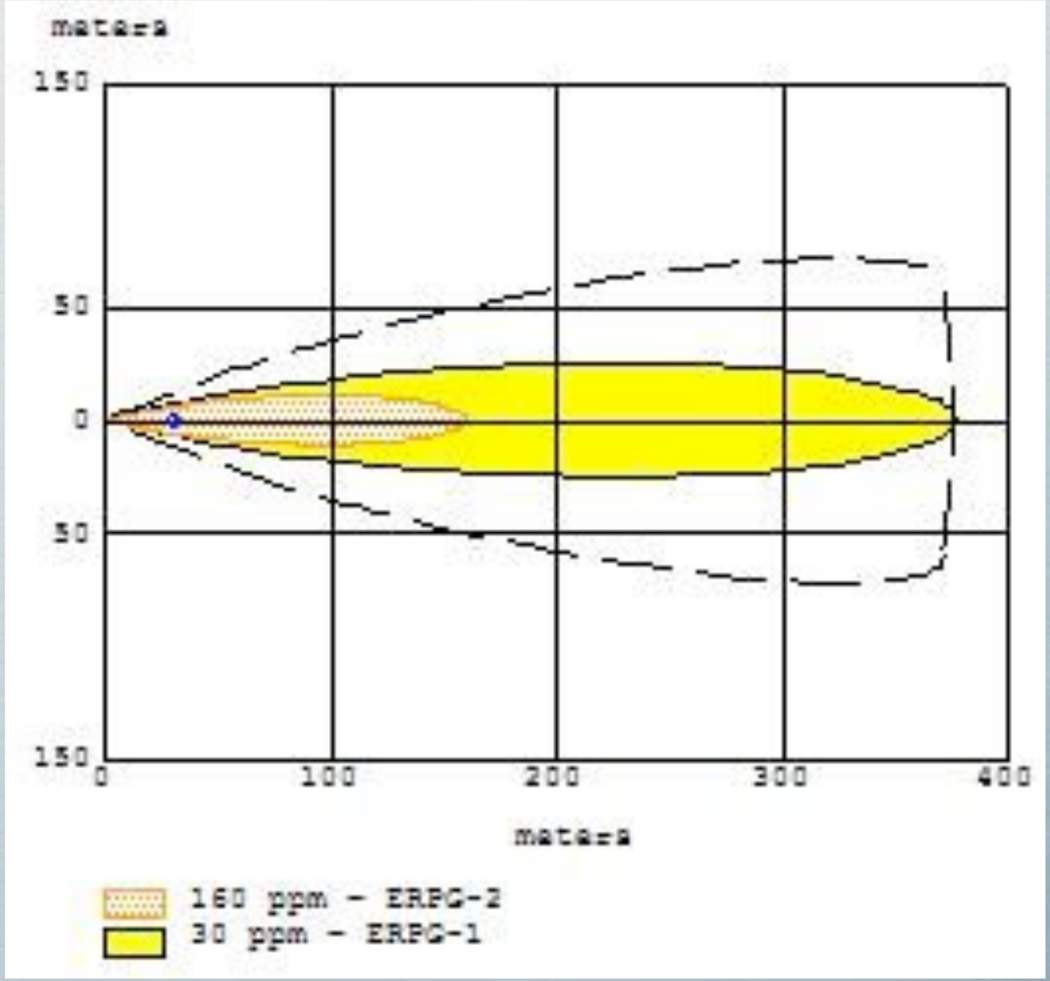
Safety Issues with Ammonia

- Toxicity vs. Asphyxiation
- Discomfort (tearing and bronchial irritation)
- Flammability
- Fixed Facility Regulations
- DOT Regulations

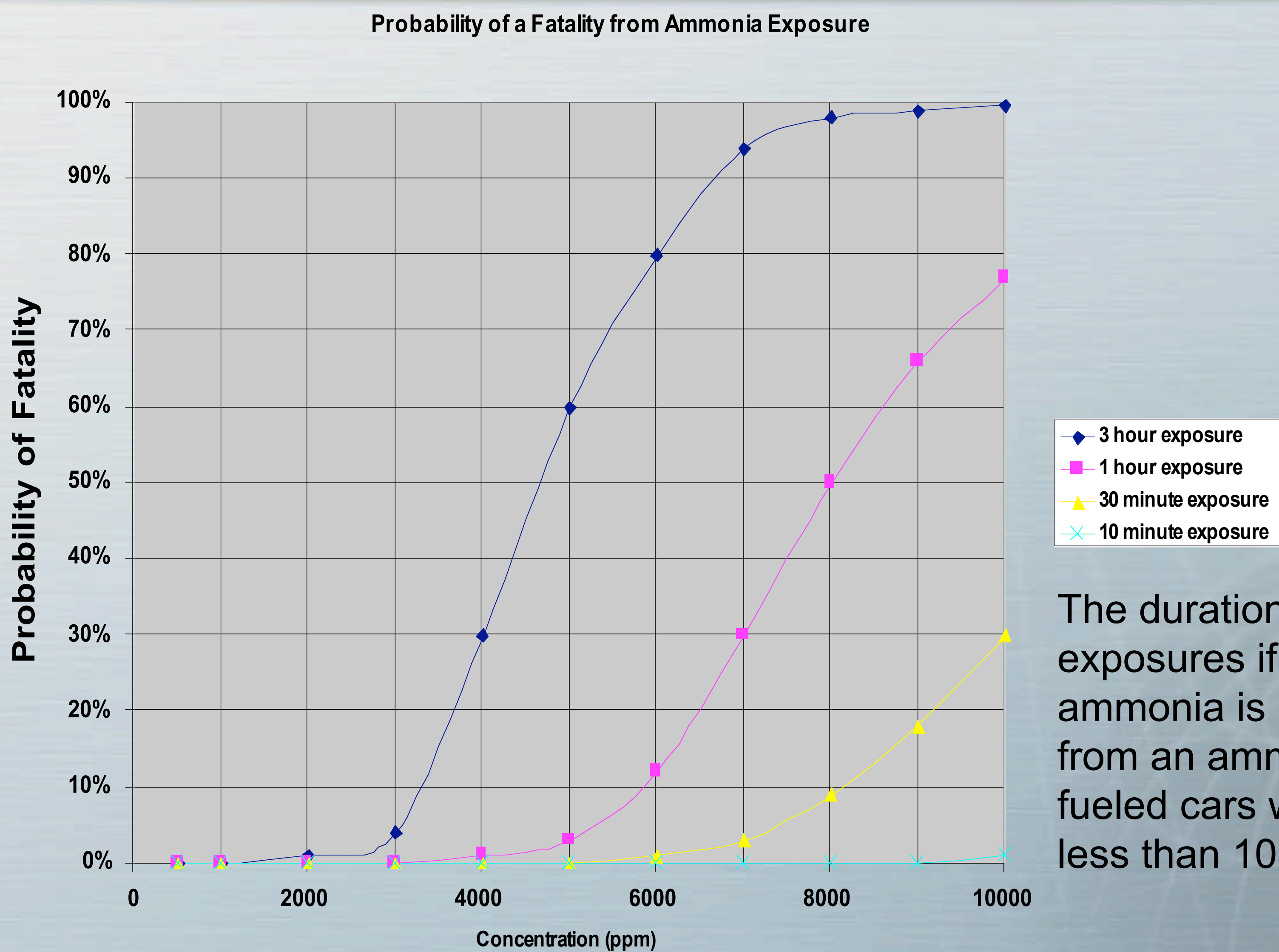
Toxicity versus Asphyxiation

- Lighter than Air
  - Molecular Weight of 17 versus Air 29
  - If at temperature of environment will disperse rapidly
- Heaver than Air when released
  - Released at normal boiling point of -33 °C (-27 °F)
  - Pressure at 21 °C – 8.8 atm., 114 psig
  - If breach is in vapor space, flashing will leave about 80 percent behind as boiling liquid
- Toxicity poses a greater hazard

Plume for a 25 gallon release over 3 minutes – daytime stability



Toxicity



The duration of most exposures if ammonia is released from an ammonia fueled cars will be less than 10 minutes

Discomfort

- Tearing and Irritation of Bronchial Passage at about 100 ppm.
  - Concern would be sensitive populations – asthmatics
- Frost bite a hazard if person comes on contact with spray of ammonia being released to atmospheric pressure or the piping upstream of the release
- Odor Threshold of 1 to 5 ppm.
- Although direct release will kill plants because of low temperature, once dispersed, ammonia is a widely used fertilizer
- Limits and Short Term Effects
  - ACGIH Short Term Exposure Limit – 35 ppm
  - NIOSH 10 hour exposure limit – 25 ppm
  - Definite irritation – 125 to 135 ppm
  - Immediate Irritation – 700 ppm
  - Respiratory Spasms, Coughing and Foaming – 1500 ppm and above
  - ERPGs 2 – 160 ppm - if below 160 ppm no difficulty evacuating plume – 1 hour exposure – no long term effects of exposure
- Affected Area based on 25 gallon release (ERPG-2)
  - Less than 2,500 m^2
  - Less than 170 m from release point exceeds ERPG-2 concentration limit but not the 60 minute part of the limit

Flammability

- Very Narrow Flammability Range
  - 15 to 28%
- Because of Volatility, concentration at release point must be assumed to be above 28 percent so there will be a point in the release plume where the released gas is in the flammability range.
- The energy required to ignite ammonia vapors is very high
- Of all the fuels, ammonia has the narrowest flammability range and highest ignition energy

Fixed Facility Regulations

- Ammonia classified as an extremely dangerous substance by EPA
- Regulated by OSHA and EPA
  - Threshold quantity for both – 10,000 pounds, about 1900 gallons
  - Production and Storage Facilities will have to have a EPA Risk Management Plan (40 CFR Part 68) – generic plans already exist for cold storage facilities and also for ethanol facilities.
    - EPA requires a worst case release scenario be presented to the affected public and be on file with emergency response personnel
  - Production and Storage facilities must also meet all OSHA requirements of 40 CFR 1910.119.
    - OSHA requires written procedures, a documented hazards assessment, formal hazards training of workers - including contractors, a documented maintenance program, and management audits
  - While separate documentation is required, there are a lot of parallel requirements – one focuses on the public the other workers

Transport Regulations

- Classified as a Division 2.2 material – a non-flammable gas.
- Any bulk shipment containing more than 1000 pounds of ammonia must be placarded
- For International Shipments, it has to be labeled as a toxic flammable gas
- Some States, California for example, list ammonia as a PIH (poisonous inhalation hazard) and designate specific routes on which placarded quantities of PIH materials can travel. Travel from pickup and drop-off points to these routes is not restricted
- Cars containing ammonia would not be placarded but the trucks supplying the refueling stations would be placarded

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Current Level of Safety

- Accept some risk, particularly if voluntary, e.g. ammonia handlers
  - a perfectly safe airplane would never fly, it would have no fuel, fly at slow speeds and probably have a crushable skin 100 feet or more thick to protect the passengers
- Being a new application of an existing technology, people will expect it to be safer than the existing technology – be prepared to make it safer even if current technology is safe
- How safe is ammonia?

How Safe is Ammonia

- What historical data is available regarding ammonia accidents?
- What are the results of analyses of ammonia supply system risks?
- Do both the historical data and the analytical results lead to the same conclusions?

HMIRS Data on Ammonia Releases-8 yrs

Mode	PHASE	Count	DEAD	Major Injuries	Minor Injuries	Average Gallons Spilled
Truck	Enroute	61	1	3	16	973
Truck	Loading and Unloading	53	1	4	9	730
Truck	Temporary Storage and Other	26	0	0	5	389
Rail	Enroute	156	1	4	18	1867
Rail	Loading and Unloading	27	0	0	0	18
Rail	Temporary Storage and Other	14	0	1	0	686
Water	Enroute	3	0	0	1	1176
Airplane			No release incidents			

HMRIS Data for Gasoline – 8 yrs

Mode Name	PHASE	Count	Total Fatalities	Total Serious Injuries	Total Minor Injuries	Average Gallons Spilled
Truck	Enroute	671	53	18	17	3018
Truck	Loading and Unloading	1443	6	4	11	107
Truck	Storage and Other	51	1	0	0	413
Rail	Enroute	71	0	0	1	73
Rail	Loading and Unloading	2	0	0	0	500
Rail	Storage and Other	3	0	0	0	1
Water	Loading and Unloading	1	0	0	0	22050
Airplane	Enroute	66	0	0	0	0.17
Airplane	Loading and Unloading	223	0	0	0	0.23
Airplane	Storage and Other	37	0	0	0	0.16

HMIRS Data for Propane – 8 yrs

Mode Name	PHASE	Count	Total Fatalities	Total Serious Injuries	Total Minor Injuries	Average Gallons Spilled
Truck	Enroute	88	1	1	2	2350
Truck	Loading and Unloading	125	6	19	25	1457
Truck	Storage and Other	20	0	0	2	349
Rail	Enroute	32	0	0	0	1138
Rail	Loading and Unloading	5	0	1	1	1584
Rail	Storage and Other	5	0	0	0	1021
Water	Enroute	0	0	0	0	0
Airplane	Enroute	1	0	0	0	0.13
Airplane	Loading and Unloading	3	0	0	0	0.45

The vehicle supply system

Delivery Vehicle

Capacity 24 Mt

4,800 vehicle full-ups

Ammonia

Fuelled Vehicle

Range: 625 km (400 miles)

Tank: 50 kgs NH_3

Supply System Risks

- In an 1988 study, there were 42,500 rail car movements of anhydrous ammonia, assume over 60,000 now. If average distance traveled is 500 km, the fatality risk is 4×10^{-9}. The overall fatality risk about five times this number.
- Based on the previous slide, for every supply vehicle transfer there will be almost 5,000 smaller transfers to an ammonia fueled automobile
- The risk of a human error is proportional to the number of operations that must be performed. Improvements should be directed at the ammonia transfer system
- Designs which reduce the contribution of human error, e.g. quick disconnects, check valves, vacuum evacuation, etc. should be used.

Comparison of Ammonia and Gasoline Supply Risks

- Direct comparison is not possible, have rail data for ammonia and truck data for gasoline
- Based on year 2000 data, the total number of car vehicle miles traveled is 2,749,803 million miles and the average fuel consumption is 16.9 miles per gallon. Assuming a gasoline tanker truck holds 8,500 gallons, there are 2×10^7 refuelings per year. Assuming a distance of 50 km and 6.6 fatalities per year from exposure to gasoline, the transport risk associated with the hazardous nature of the gasoline is 7×10^{-9} /kilometer, about twice the comparable number for transport of ammonia by rail. The overall truck fatality risk is about three times this number.
- Considering uncertainties, rail transport of ammonia is no more hazardous than truck transport of gasoline

Comparison of Current Risks

- The previous slide shows the transport risk for ammonia and gasoline is comparable. However gasoline has additional risks. Over 9 million people live in areas were the carbon monoxide concentration exceeds the EPA guidelines of 9 ppm over 8 hours and 35 ppm over one hour at least one a year. Ninety percent of these emissions are attributed to automobiles. In addition, the estimated number of fatalities from auto emissions is 1500 people annually
- Ammonia would not present these risks

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For truck the ratio of transfer and enroute incidents much higher than rail, reflecting the greater number of transfers to smaller vessels. Fueling cars with ammonia with no technological improvement would make the loading and unloading releases even more dominant

What does current experience say

- Over an eight year period, the two fatalities occurred from transport accidents, releases large, many times the amount in a car running on ammonia.
- Releases during transfer seem particularly high
- The one transfer fatality shows the ammonia can be toxic in small quantities. In the one filling fatality reported in HMIS, operator closed the valve on the supply tank and nurse tank but did not close the valve on the flexible hose, a half a gallon of ammonia sprayed into his face and chest when he disconnected the supply hose. (the 6/5/05 fatal accident not reported to DOT)
- Simple fitting changes (quick disconnects with shutoff or vacuum evacuation of the line – the Danish recommendation) would have prevented this fatality.

Danish Study of Ammonia Risks in Comparison to other fuels

- The Danish analytical study compared the risk of using ammonia, gasoline, propane, methanol and propane as an automobile fuel
- Performed FMEA, HAZOP and quantitative risk assessments for the ammonia supply chain. The transport of fuel to the fueling station posed the greatest risk
- Ammonia had the highest risk because of the calculated distance to the point where there is a 10 percent chance of a fatality to a single individual.
  - The suggested safety fix was to refrigerate the ammonia in the refueling truck
- The risks associated with releases from the automobile were more similar for all fuels

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Danish Study of Ammonia Risks in Comparison to other fuels

- It is very difficult to model the consequences of small releases because the impact zone is very small and the models very uncertain. The report admits the uncertainty and suggests that only the relative risks are valid.
- Concluded that when the safety measures were applied, the use of ammonia as a transport fuel wouldn't cause more risks than currently used fuels (using current practice)
- The Danish set a goal of a very low rate of failure of the ammonia fuel tank, 2×10^{-4} per fatality.
  - As a comment on this goal, fuel tank failure does not seem to be a major contributor to the overall risk of using ammonia – the releases during filling caused by human error dominate the risk

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Do the Analytical Results and Current Experience reach the same Conclusions

- While there are differences, overall the answer is yes
  - Both conclude that there are manageable risks associated with the utilization of any fuel
  - Both identify areas where the the application of current technology will lower the risk
- The overall conclusion is that lowering the risk is important if the public is going to accept a new application for ammonia

Some Buried Nuggets in the Analyses

- In the Danish study, it was stated that the fuel tanks used in propane fueled vehicles had not failed in any accidents and the vehicles had been driven over 50 billion kilometers. Since the ammonia fuel tanks have many of the same design characteristics, similar performance can be anticipated for vehicles fueled with ammonia
- Based on a limited study of HM cargo tanks accidents, gasoline cargo tanks rupture was common. These resulted in large releases
- In a brief look at the ammonia releases, the vast majority were from valve failures. In 20 transport accidents, 13 releases, averaging 1300 gallons were from valve failures, there was one puncture releasing 1800 gallons and the rest were either leaks enroute or the cause of the release was not specified.

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Integrate Safety into System

- Review what others have done and use cost benefit analyses to select the optimum set of safety systems
- Consider vapor recovery systems during filling
- Underground tanks and buried piping probably safer than above ground tanks and piping – double walled?
- Ammonia has a tremendous affinity for water – use it to advantage
  - Passive systems more reliable than active systems
    - Fill vehicle on a grate with a water pool underneath
    - Use a natural convection system to dissipate any small ammonia releases
  - Active systems can be a backup for larger releases
    - Water sprays
    - Active Ventilation systems
- The risk data clearly show that the operations that could most be improved are the ammonia handling operations at the refueling station
  - Cost benefit analyses should be used to identify those pieces of handling equipment and safety systems that would make the ammonia transfer operations more fail safe.

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Inherent Safety

- A Way of Thinking
- Consider
  - Minimizing Amount of Ammonia
    - Segmentation might be permitted if tanks not connected
  - Substitute a less hazardous material
    - Urea
  - Moderate
    - dilute the ammonia in water
  - Simplify
    - complex systems might not be safer
    - passive safety preferred over active safety systems
      - Natural convection versus forced ventilation or water sprays
    - prevention preferred over protection over mitigation
- Inherent safety approaches frequently cost effective as well

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Summary and Conclusions

- Ammonia is easy to contain, doesn't require exotic or high tech storage/delivery systems, and safe handling systems and procedures currently exist
- For public acceptance, the small nuisance releases, with no health effects, will be a problem and must be reduced to a minimum. Some systems development might be required in this area
- While the risks of handling ammonia are different from gasoline and propane (toxicity as opposed to fire) the risks of handling all three commodities are small and very manageable.
- Improvements, such as the use of new handling equipment (better quick disconnects?) or safety systems (passive ventilation?) should be subjected to cost-benefit analysis before implementation

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