Ammonia safety, a global perspective.

M. Kent Anderson

President Emeritus, IIAR

Past Chair, ASTI

AMMONIA - AS NATURAL AS WATER

©

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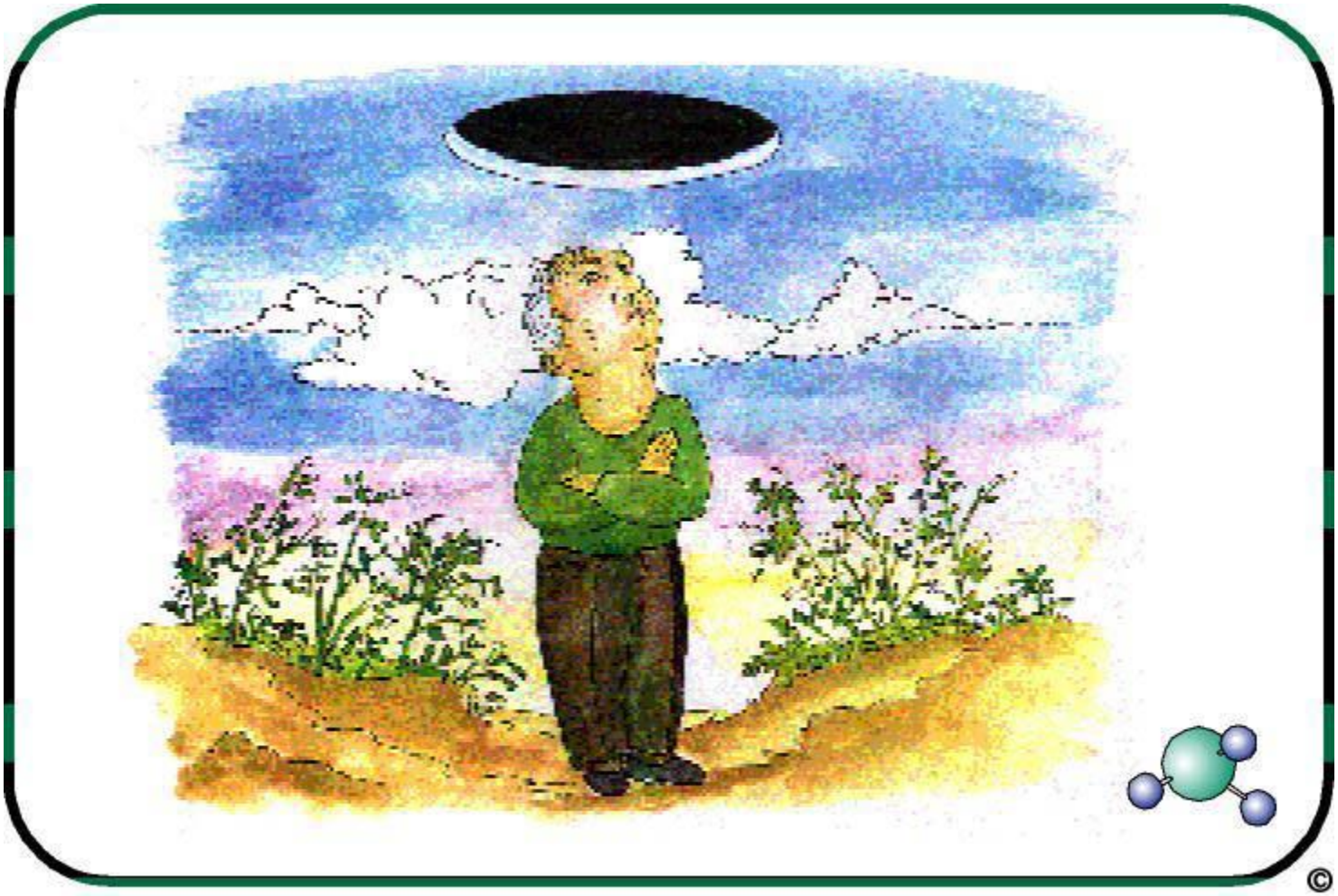
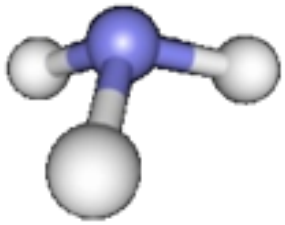
In the beginning NH_3 was the catalyst for life

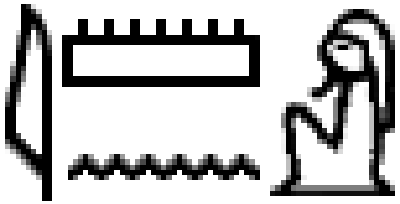
Technion Ammonia Conference. November 2017

We are in the beginning of environmental change
Ammonia will be needed more in the future!



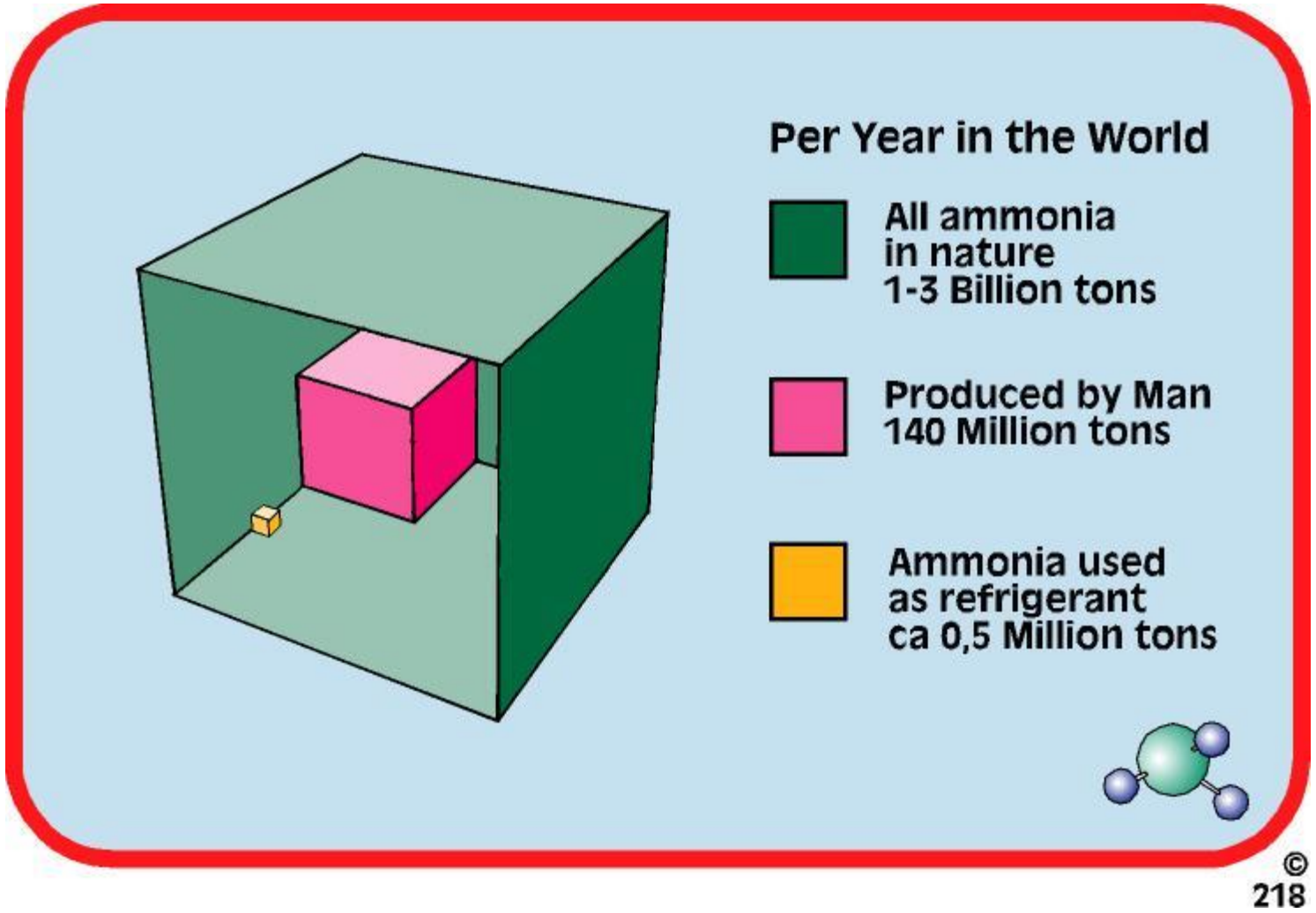
Ammonia: What's in a Name?





- Sal Ammoniac
  (Salt of Ammon)
- Spirit of Hartshorn
- Ammoniak/Ammoniac
- NH3
- Anhydrous Ammonia
- אַמוֹנְיָה

"What's in a name? A rose by any other name would smell as sweet", William Shakespeare, Romeo and Juliet – Act II, Scene II


Per Year in the World
All ammonia in nature 1-3 Billion tons
Produced by Man 140 Million tons
Ammonia used as refrigerant ca 0,5 Million tons
©
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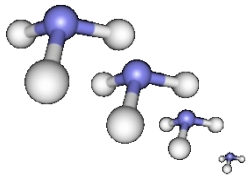
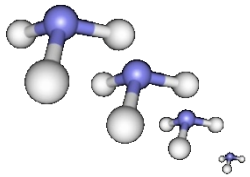


Ammonia Production/Use

- **145 million metric tons of ammonia produced per year**
  - **China = 50 million metric tons**
  - **Russia = 12 million metric tons**
  - **India = 11 million metric tons**
  - **United States = ~10 million metric tons**
  - **Israel = ~120 THOUSAND metric tons (0.1% of world production capacity)**



Ammonia Uses

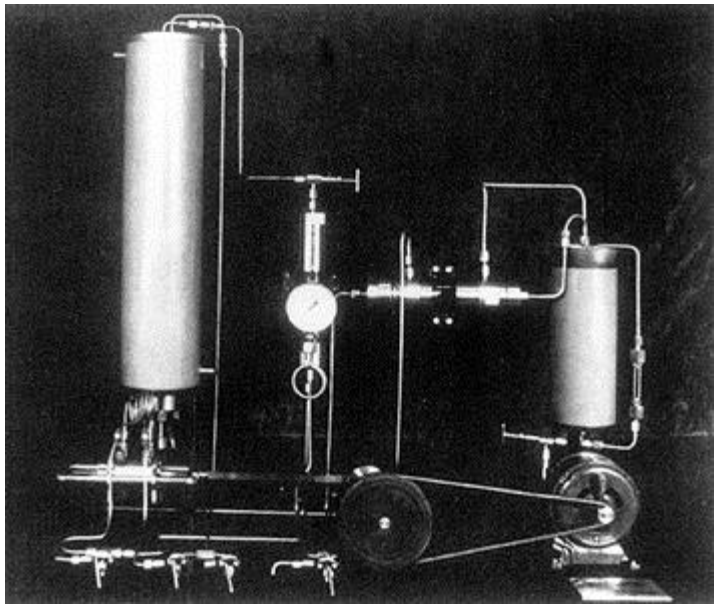
- **80 % agricultural use**
- **18 % in industrial processes**
- **<2 % as a refrigerant**

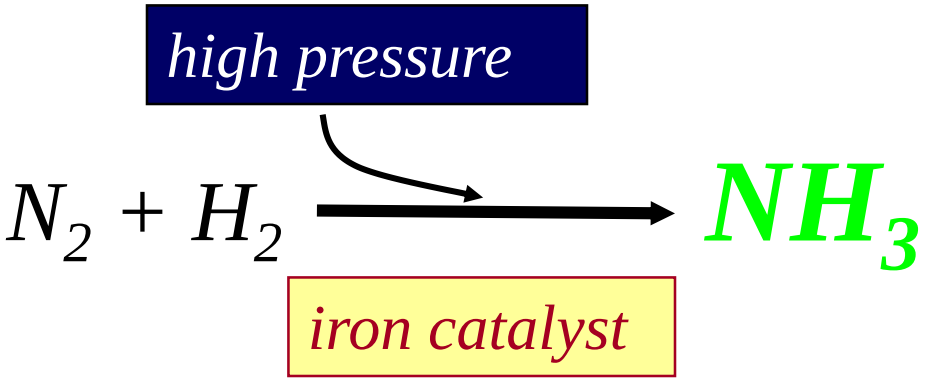
Chilean saltpeter (potassium nitrate)

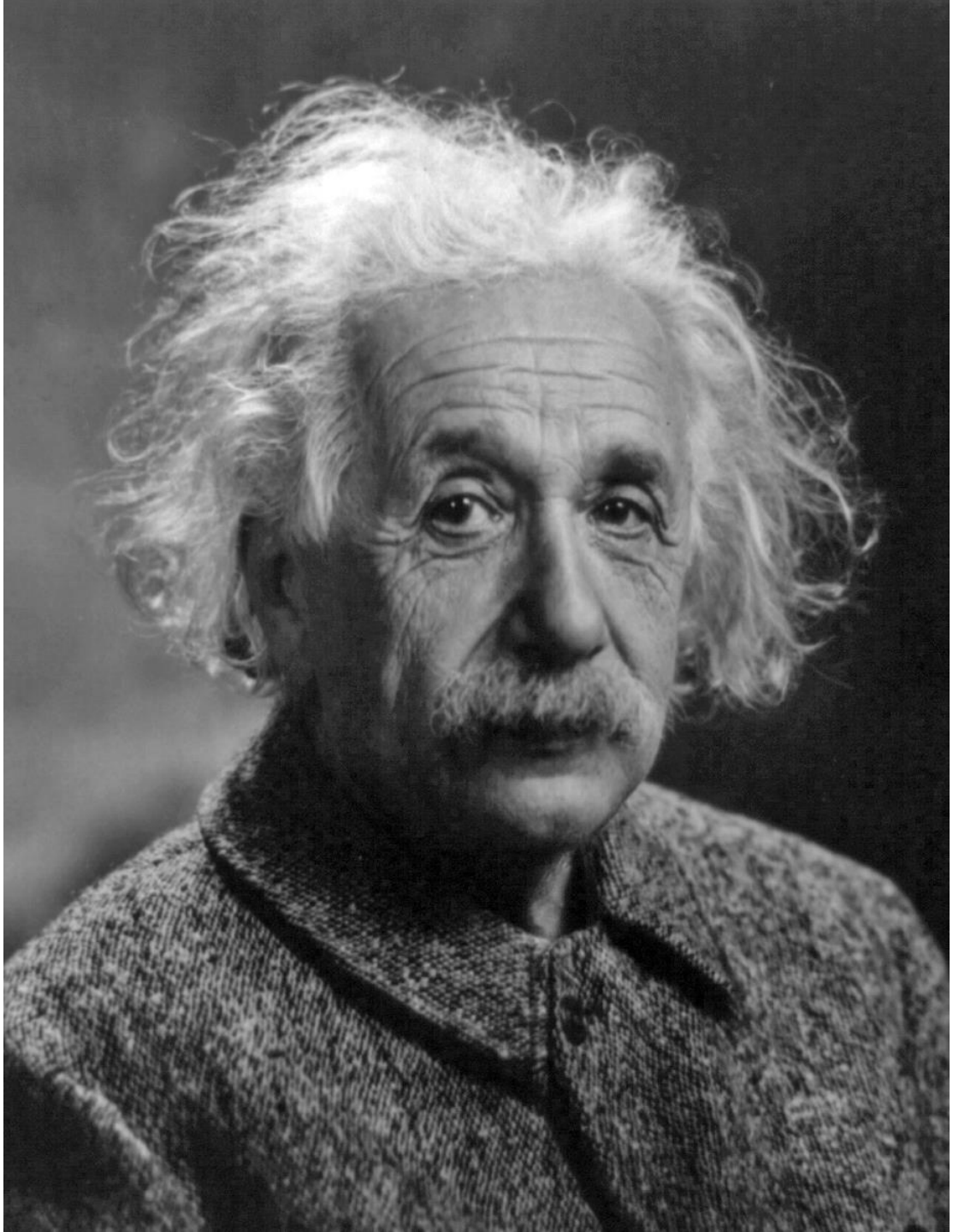
Peruvian guano

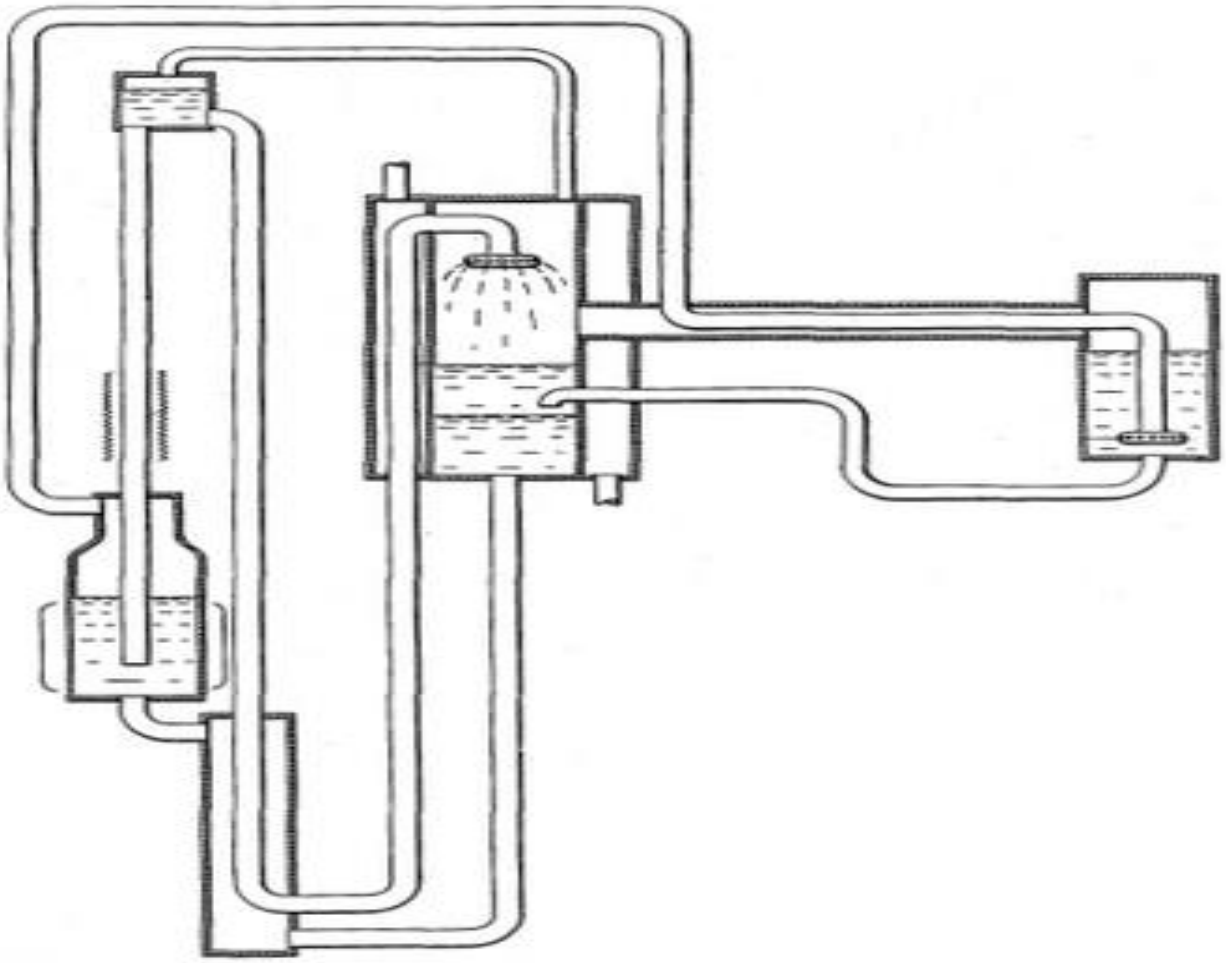
Fritz Haber

Carl Bosch









Einstein Refrigerator

Patent number US1781541 -- November 11, 1930

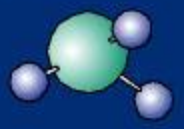
Albert Einstein

Leo Szilard

Dr Mark Mc Linden Study for NASA 1988

860 chemicals were studied

- Application
- Liquid/gas physical properties
- Thermophysical properties
- Stability
- Toxicity
- Flammability
- Compatibility to materials, gaskets, oils....
- Price



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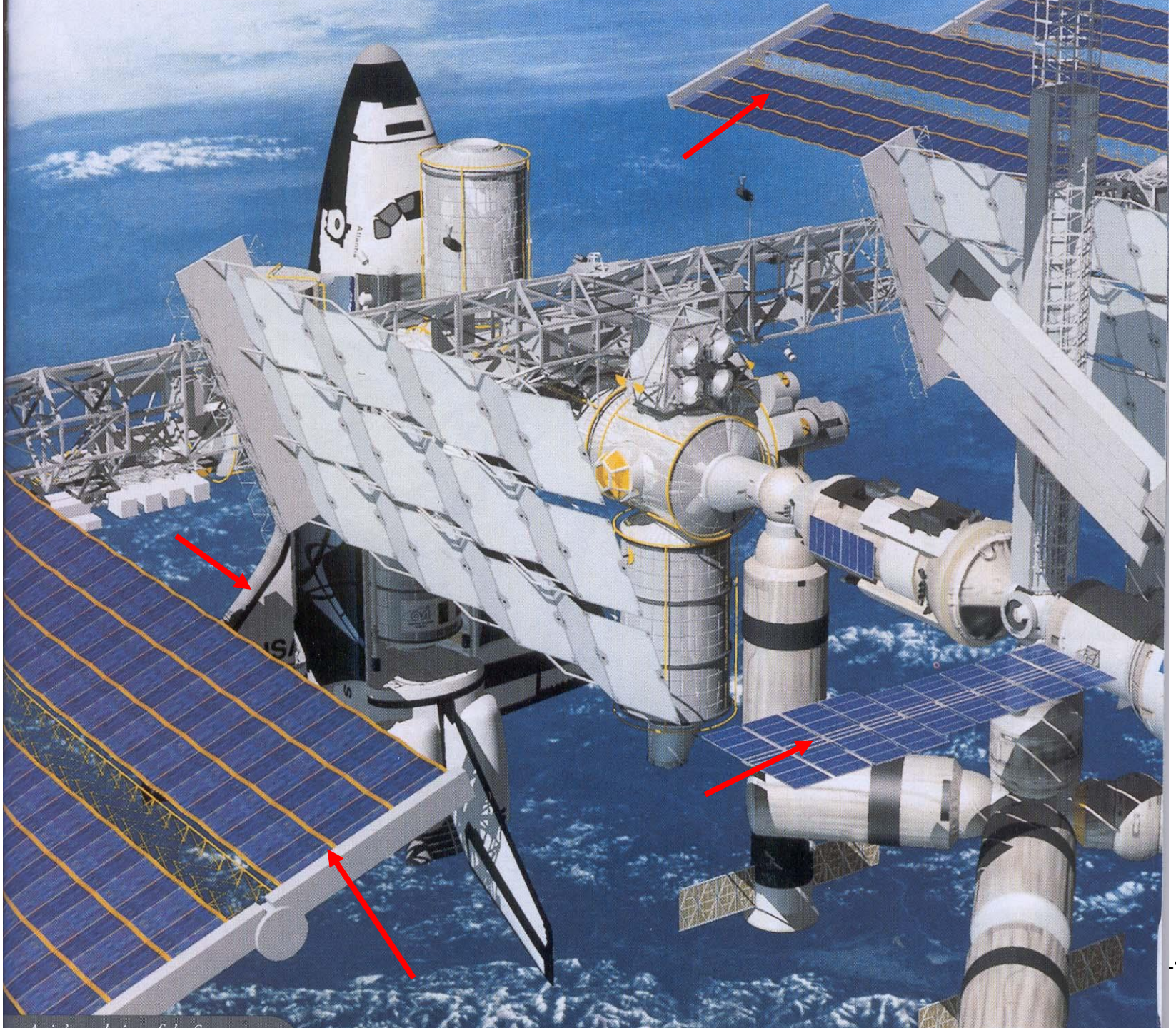


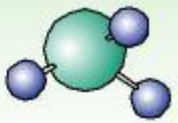
Ammonia

— was considered the best and most appropriate followed by:

— Propane R 290, methylamine R 630, isobutane, R 152 a, R 22, Halon 1301 or R 13 B1, R 12 and R 11.

— The investigation shows that the better chemicals are simple molecules.

— It is not likely that there are other chemicals with
- better refrigeration performance.
- lower manufacturing costs.
- better toxicity and flammability properties.
- lower or no global environmental influence, ODP and GWP.



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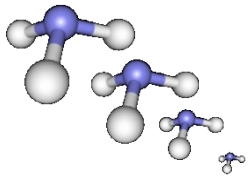


Ammonia Safety
Hazards, Risks and Threats

Hazards (Properties)

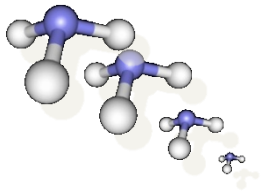
- Chemical
- Physical
- Thermodynamic

Risks

- Life
- Environment
- Product, Equipment, Processes

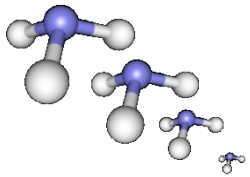
Threats

- Fire
- Overpressure
- Releases
- Reactivity
- Other (Natural, Terrorism, etc.)



Keys to Ammonia Safety

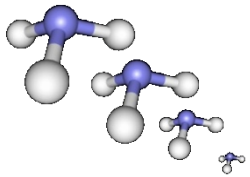
- Understand the Hazards
- Manage the Risks
- Control the Threats



Ammonia
Physical Properties[1]

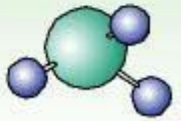
Physical state	*Colorless gas at NTP*
Formula	*NH3, H3N*
Molecular Weight	*17.03*
Gas-density to dry air	*0.60*
Freezing temperature	*-108°F (-78°C)*
Boiling temperature	*-28°F (-33°C)*
Ignition temperature	*1,204°F (651°C)*

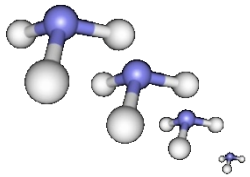
[1] atmospheric pressure



THE GASES LIGHTER THAN AIR

Hydrogen	H	0,07
Helium	He	0,14
Methane	CH_4	0,55
Ammonia	NH_3	0,59
Hydofluoric acid	HF	0,59
Neon	Ne	0,70
Acetylene	C_2H_2	0,91
Hydrocyanic acid	HCN	0,93
Carbon monoxide	CO	0,97
Nitrogen	N_2	0,97
Etylene	C_2H_4	0,98

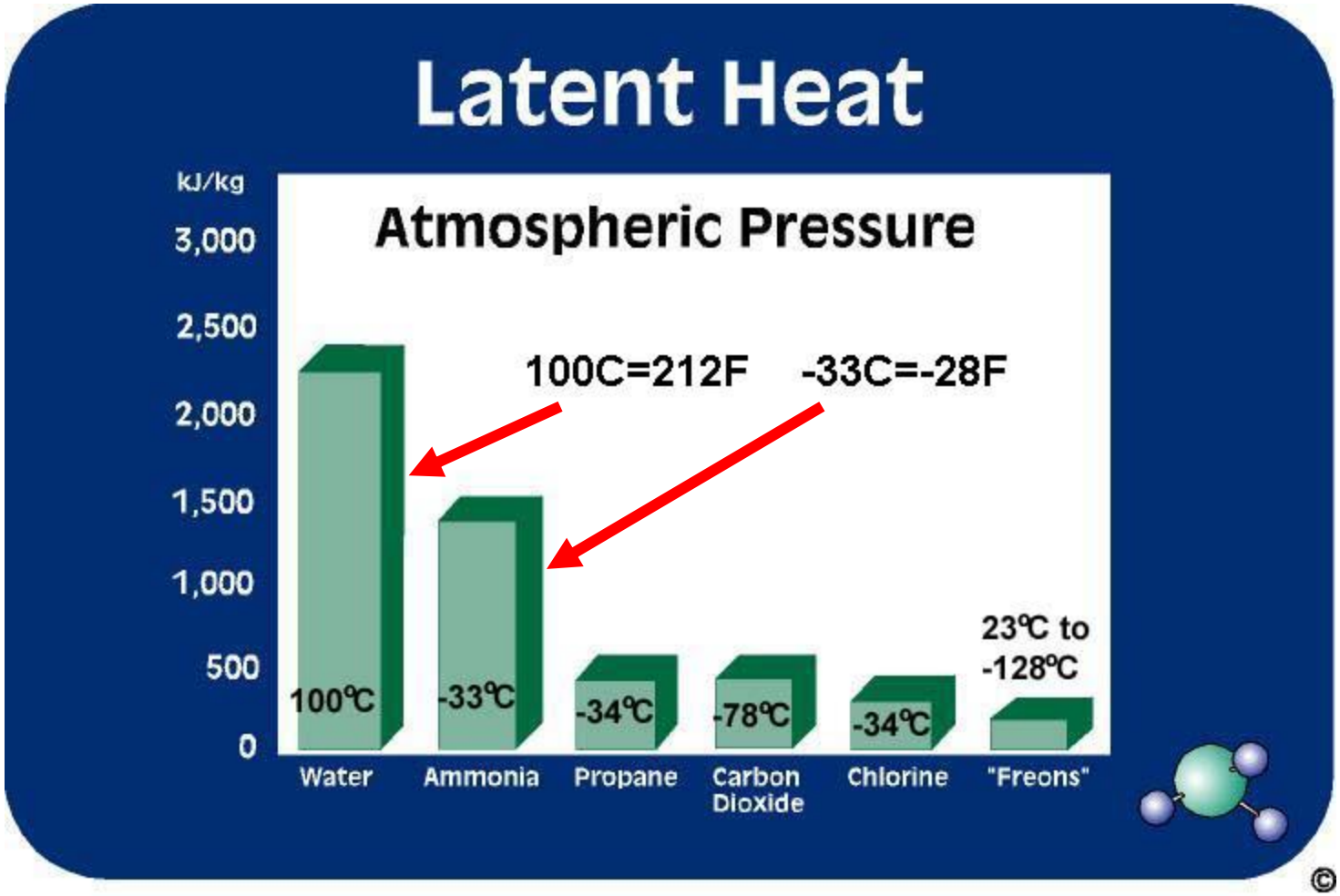




Ammonia
Chemical Properties[1]

Heat of combustion	*7,992 Btu/lb (4,440 kcal/kg)*
Heat of formation	*-10.96 kcal/mole*
Latent heat	*588 Btu/lb (327 Kcal/kg)*
Toxicity	*Toxic Inhalation Hazard*
Flammable conc. in air in confined space	*15-28 % volume*
Ignition temperature	*1,204°F (651°C)*

[1] atmospheric pressure


Latent Heat
kJ/kg
3,000
2,500
2,000
1,500
1,000
500
0
Atmospheric Pressure
100C=212F
-33C=-28F
100℃
-33℃
-34℃
-78℃
-34℃
23℃ to
-128℃
Water
Ammonia
Propane
Carbon Dioxide
Chlorine
"Freons"
©
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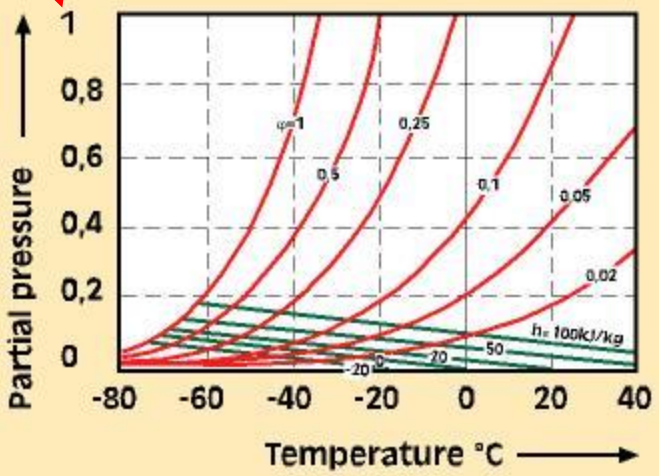
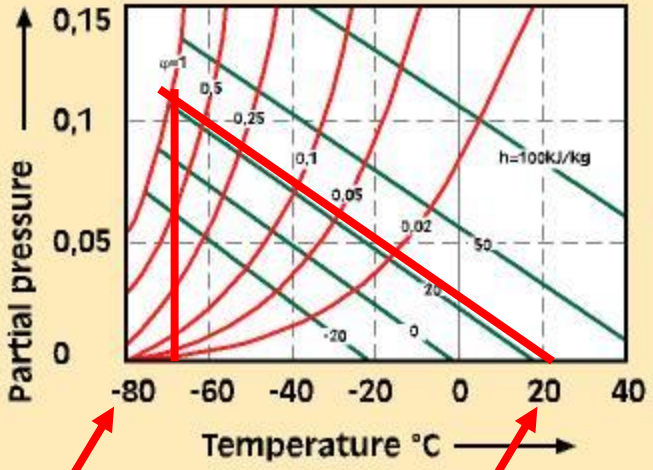
Atmospheric Pressure

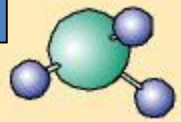
NH_3 in atmospheric air





-94ºF

68ºF



©
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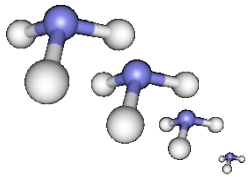


Ammonia Toxicity & Flammability

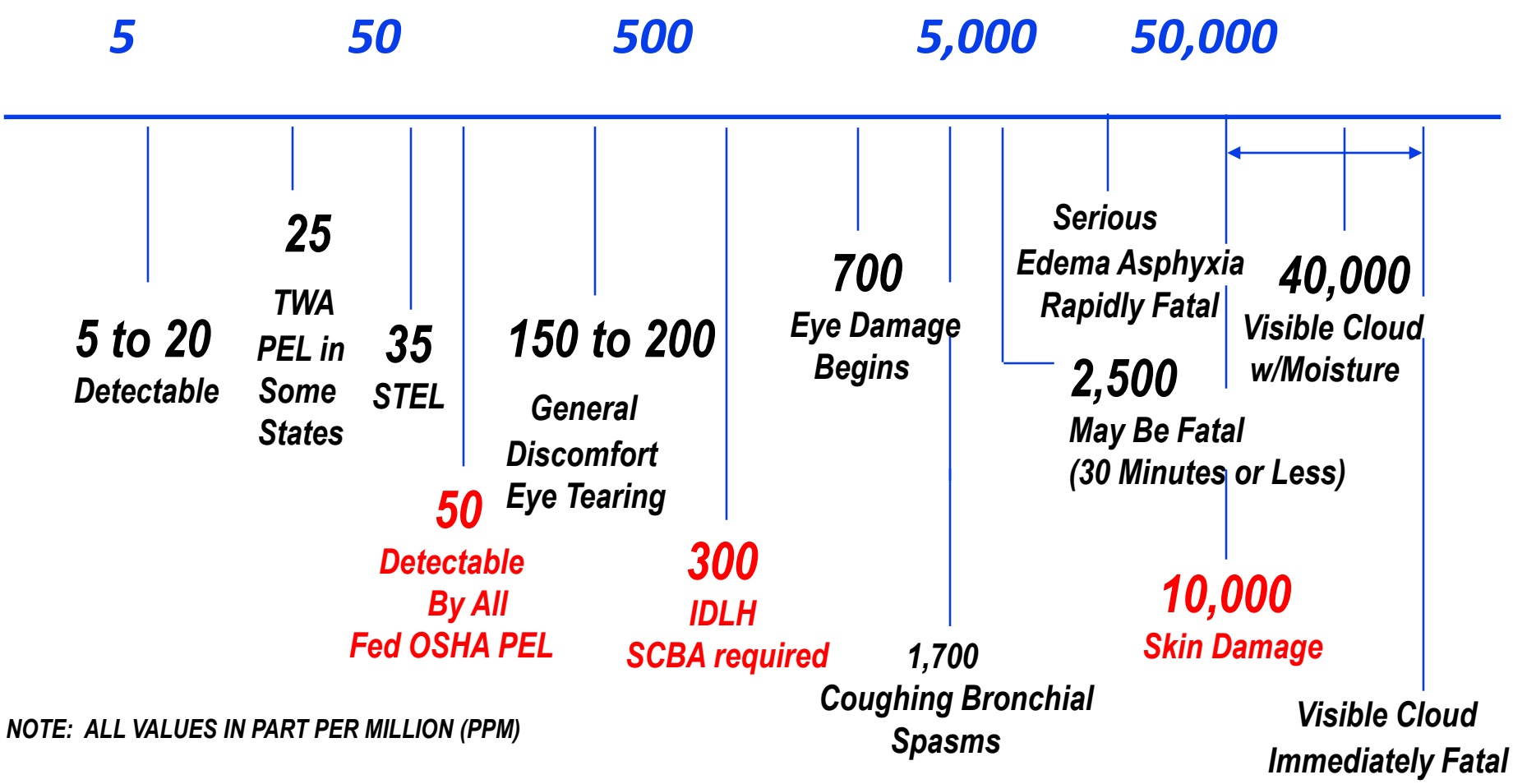
- *PEL : 50 ppm*
- *IDLH : 300 ppm*
- *Odor threshold : 5 ppm to 50 ppm*
- *Above 100 ppm, uncomfortable*
- *Between 300 - 500 ppm, unbearable*

Fire and explosion hazard : concentrations of 16% to 25%+

- *Mixtures of ammonia and oil may reduce lower limit to 8%*

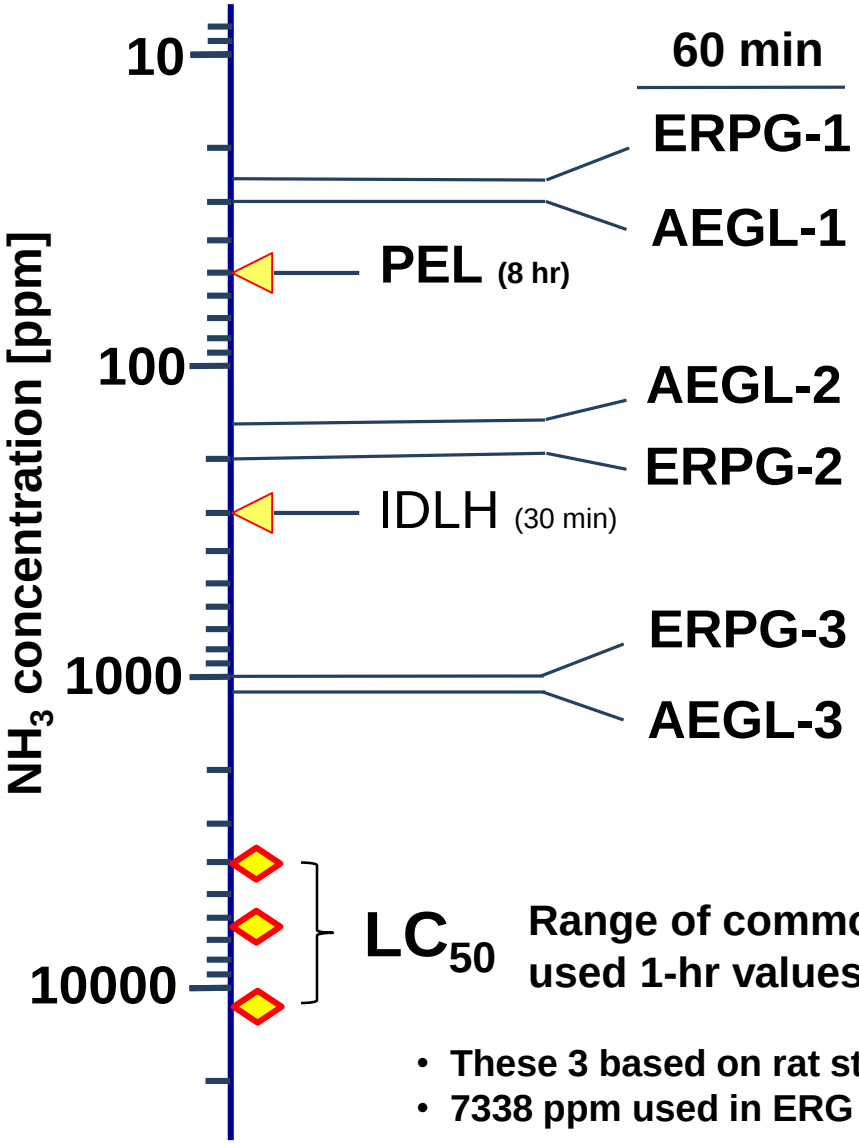
AMMONIA NH_3 SAFETY & TRAINING INSTITUTE

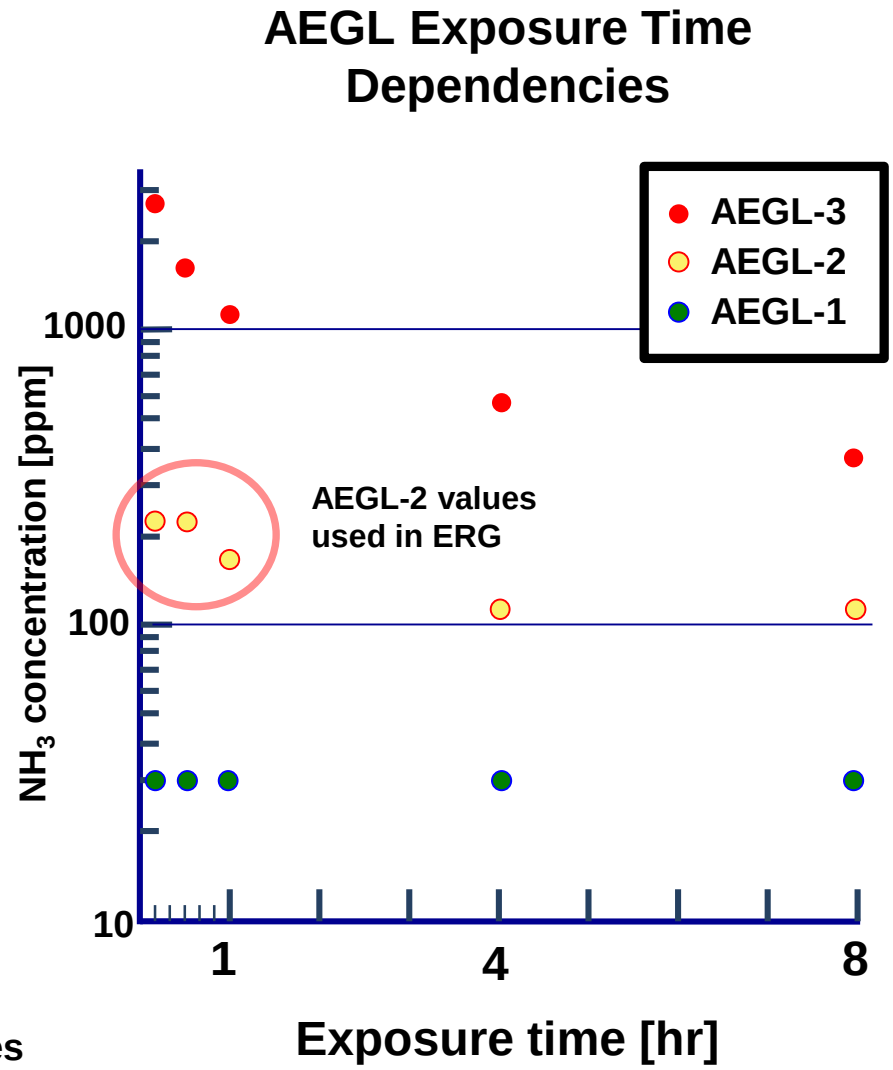
RULE OF FIVES



NOTE: ALL VALUES IN PART PER MILLION (PPM)

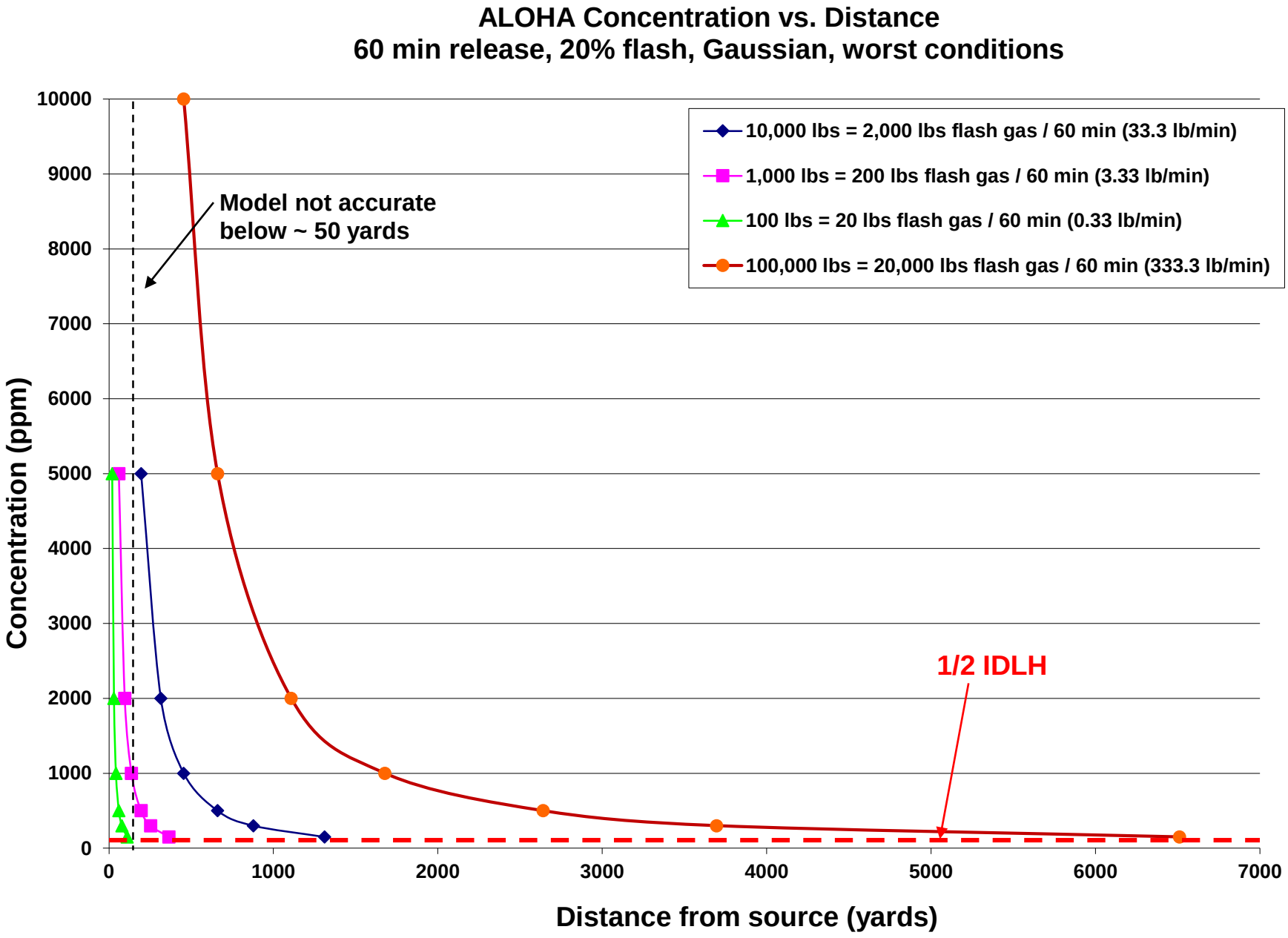
Ammonia Health Criteria

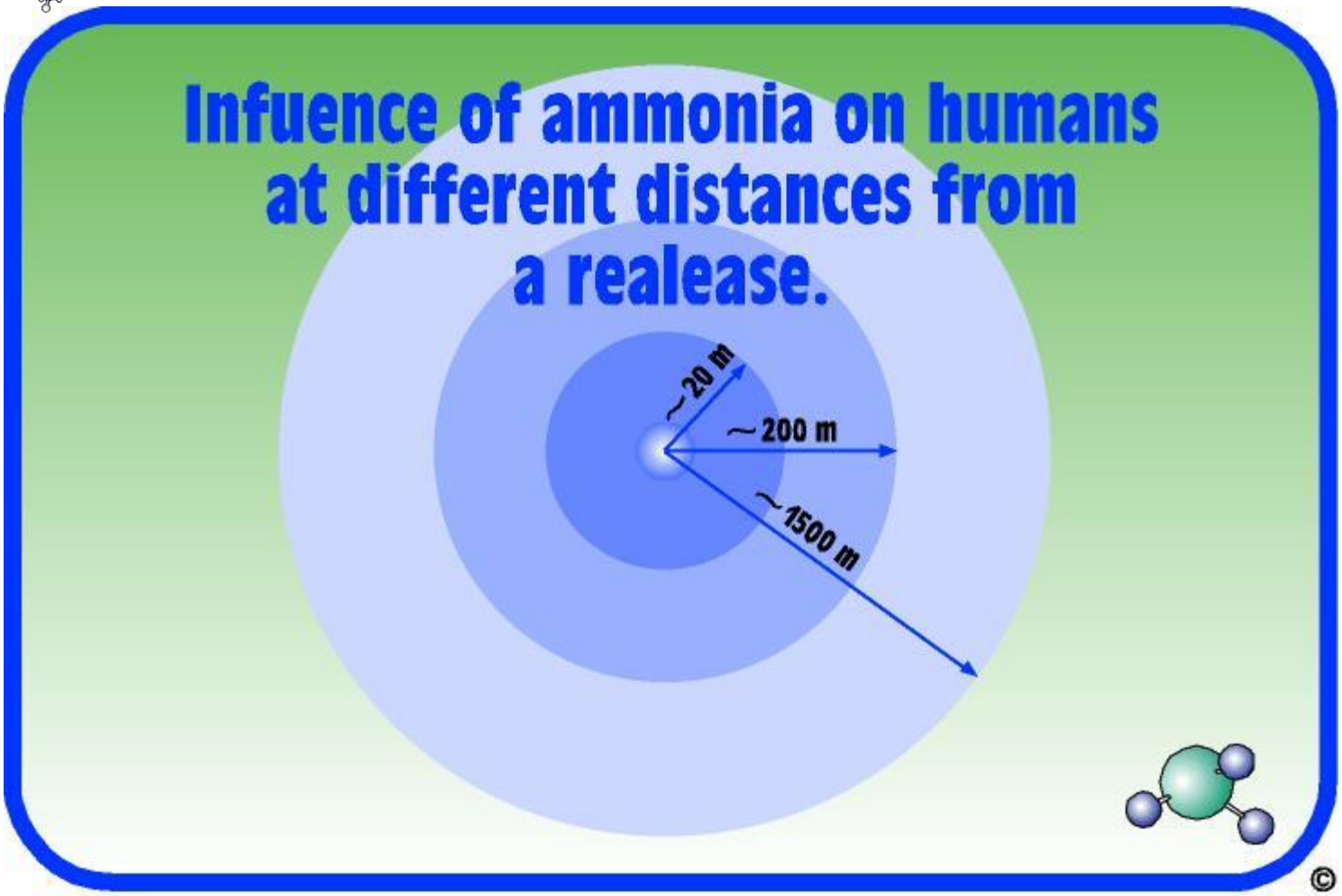




The most basic tenant of toxicology: *The dose makes the poison*.

- "All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy."
- Paracelsus (1493-1541)


ALOHA Concentration vs. Distance
60 min release, 20% flash, Gaussian, worst conditions
10,000 lbs = 2,000 lbs flash gas / 60 min (33.3 lb/min)
1,000 lbs = 200 lbs flash gas / 60 min (3.33 lb/min)
100 lbs = 20 lbs flash gas / 60 min (0.33 lb/min)
100,000 lbs = 20,000 lbs flash gas / 60 min (333.3 lb/min)
Model not accurate
below ~ 50 yards
1/2 IDLH
Concentration (ppm)
Distance from source (yards)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000


Infuence of ammonia on humans
at different distances from
a realease.
~20 m
~200 m
~1500 m
©
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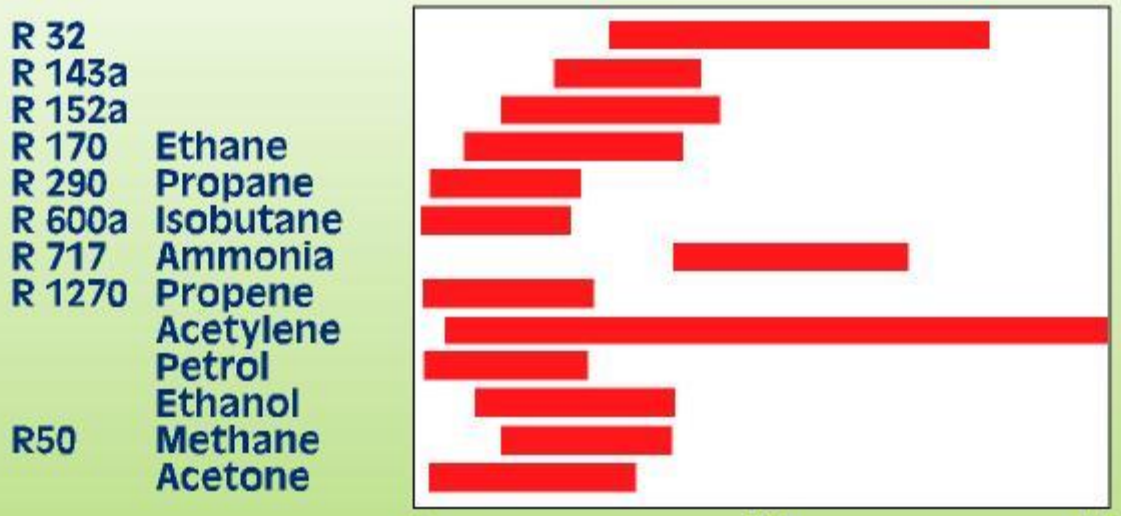
Comparison of different flammable concentrations in air



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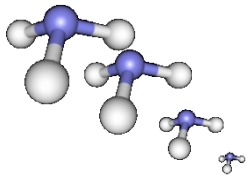
Risks

Manage Risk to:

- Life
- Environment
- Product, Equipment and Facilities



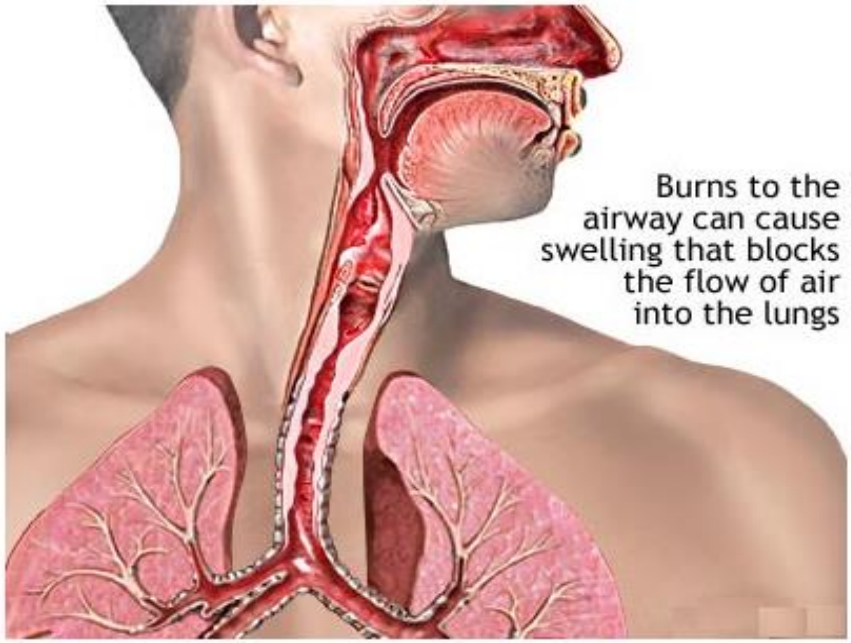
Life Risks

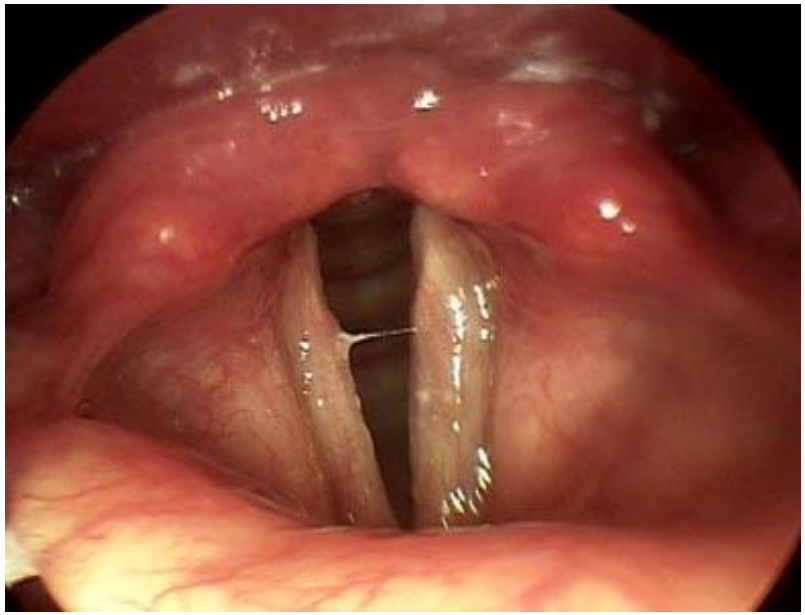
Respiratory

Exposure – skin and eyes

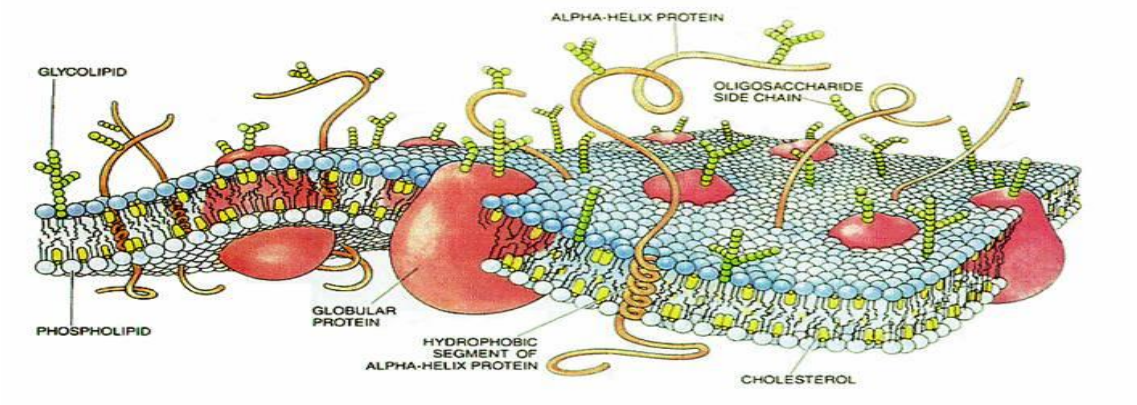
Nausea, Cardiac, Heat Stress

Respiratory - Inhalation



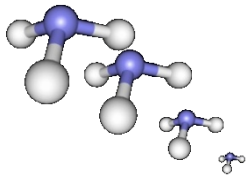


Exposure - Skin Damage



- *Critical* skin damage begins at 24.8°F and becomes irreversible at -18.5°F.
- The degree of tissue injury is proportional to the *duration* and *concentration* of exposure.
- Alkaline burns go *deeper* than acid burns.
- Alkali burns are yellow, soapy, and soft in texture. When burns are severe, skin turns black and leathery.

Exposure - Eyes



Medical Emergencies

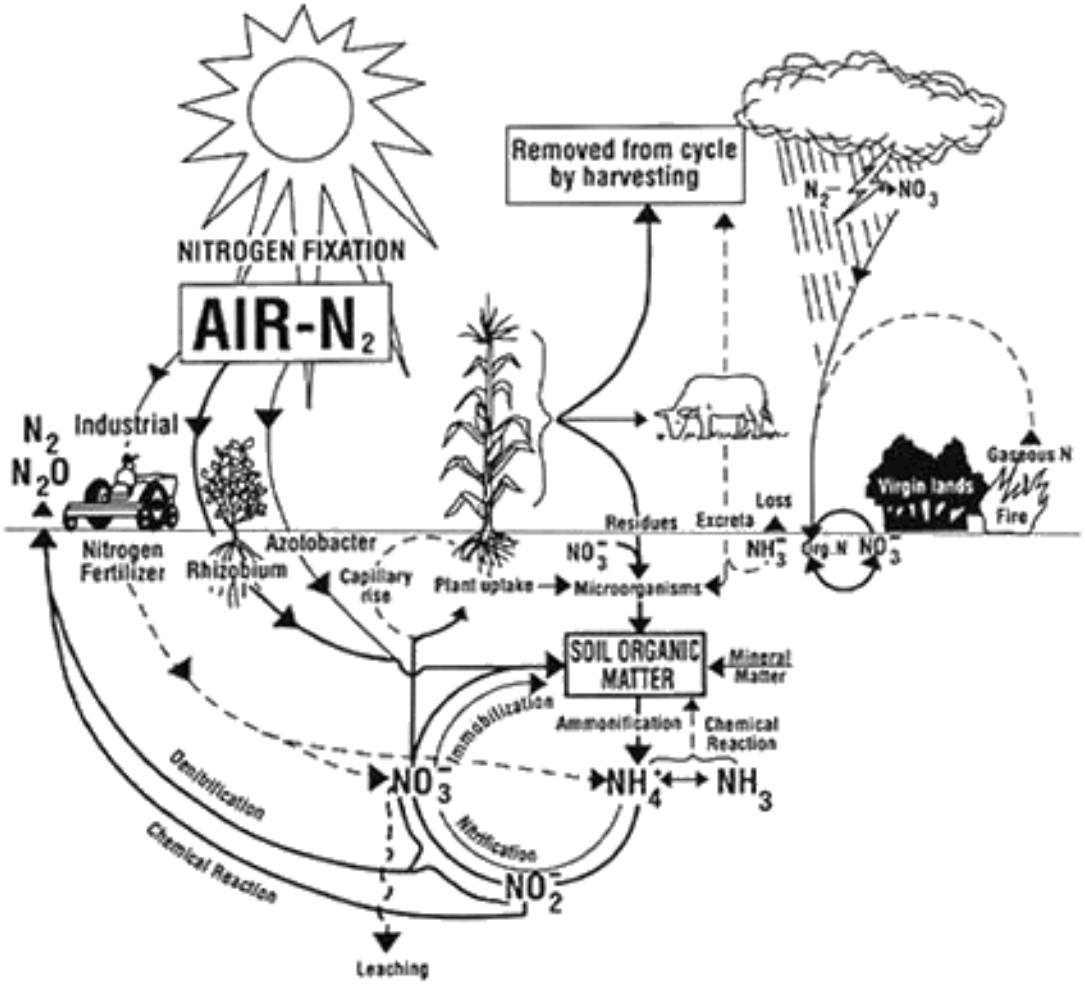
Nausea

Cardiac

Heat: Rash, Exhaustion, Stroke

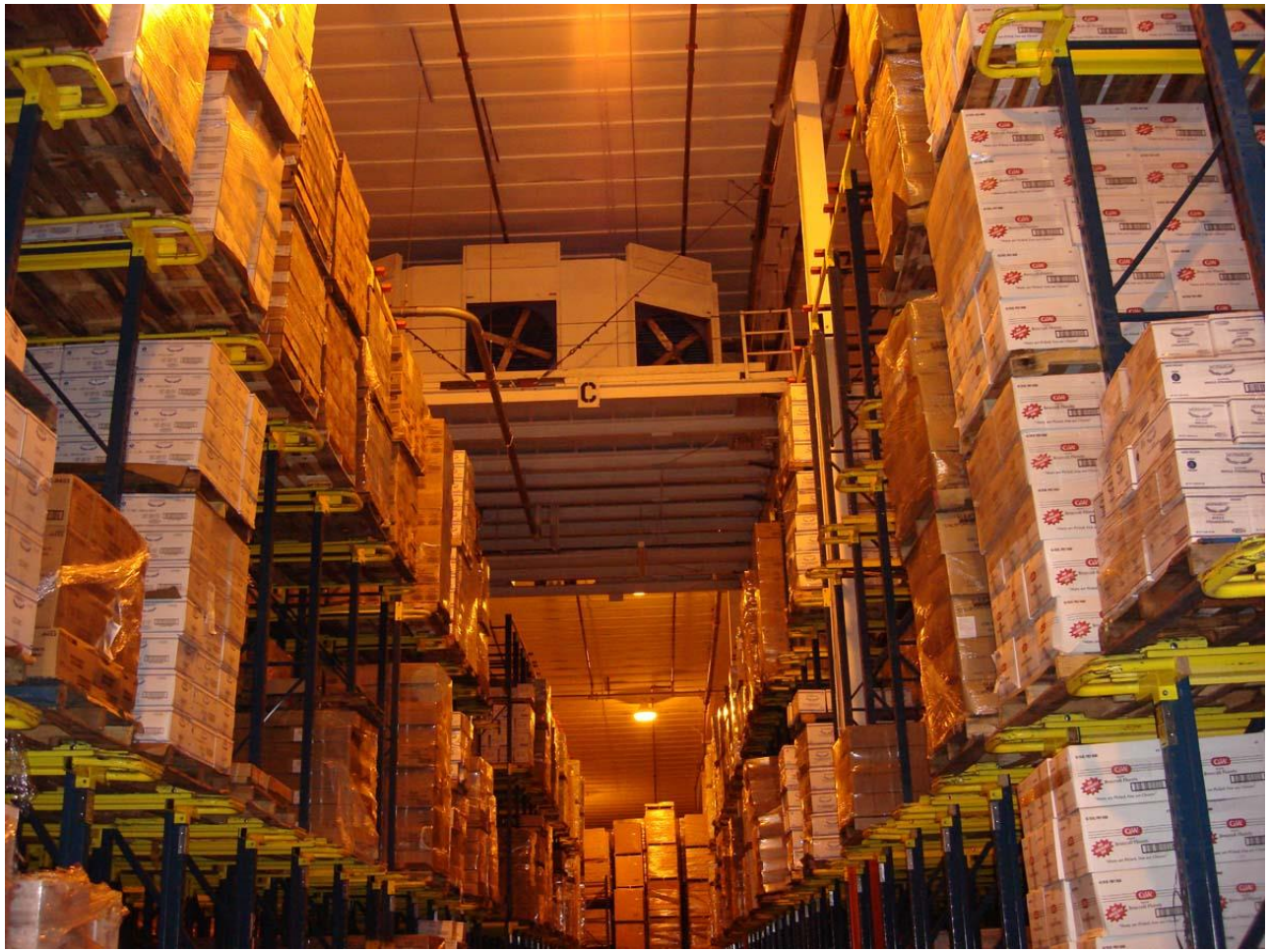
Shock

Environmental Risks

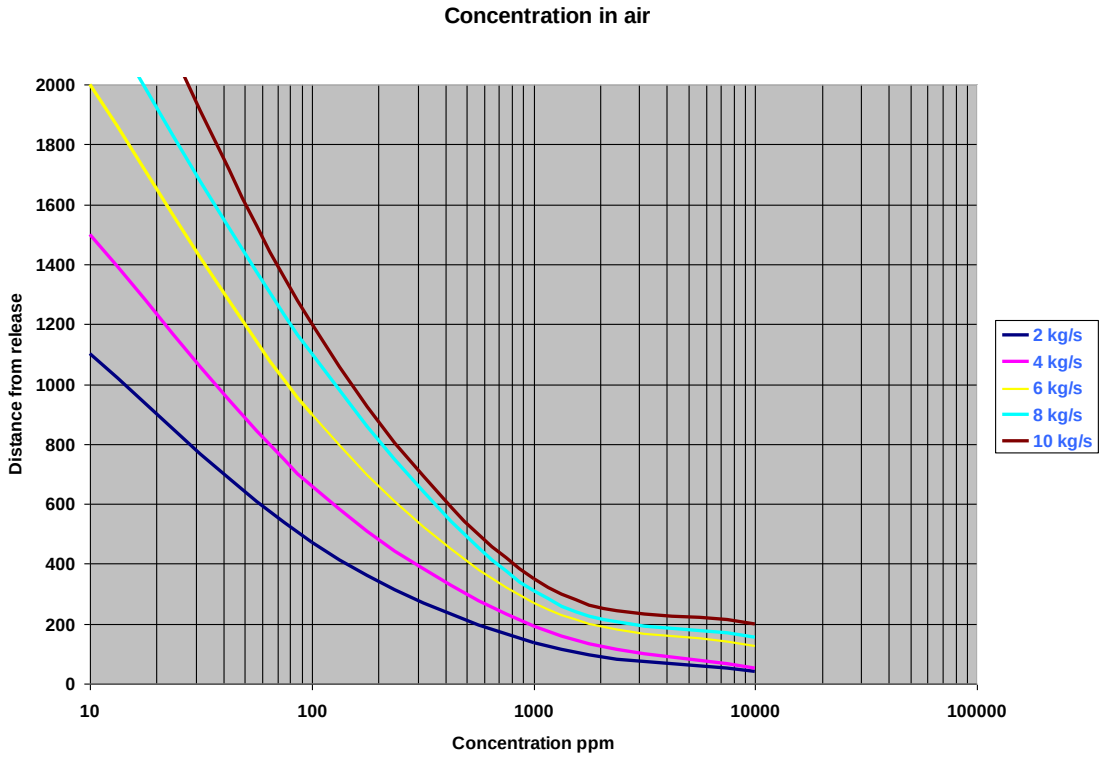


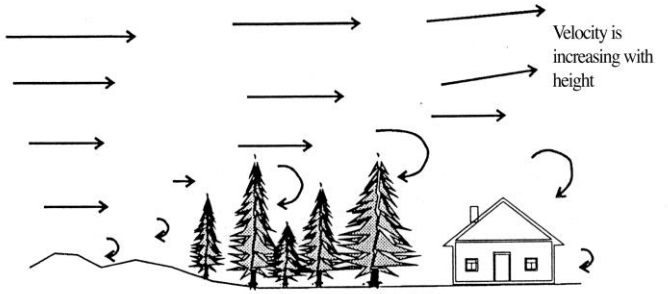
Technion Ammonia Conference. November 2017

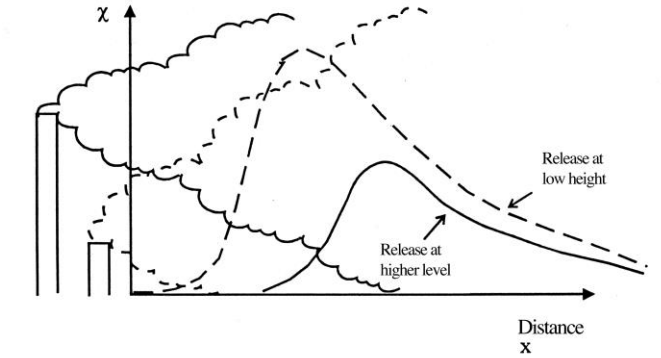
Product, Equipment and Facility Risks



Wind and Dispersion





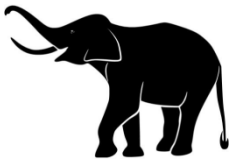


Dealing with Risks

There is no such thing as zero risk!

- Black Swans[1]

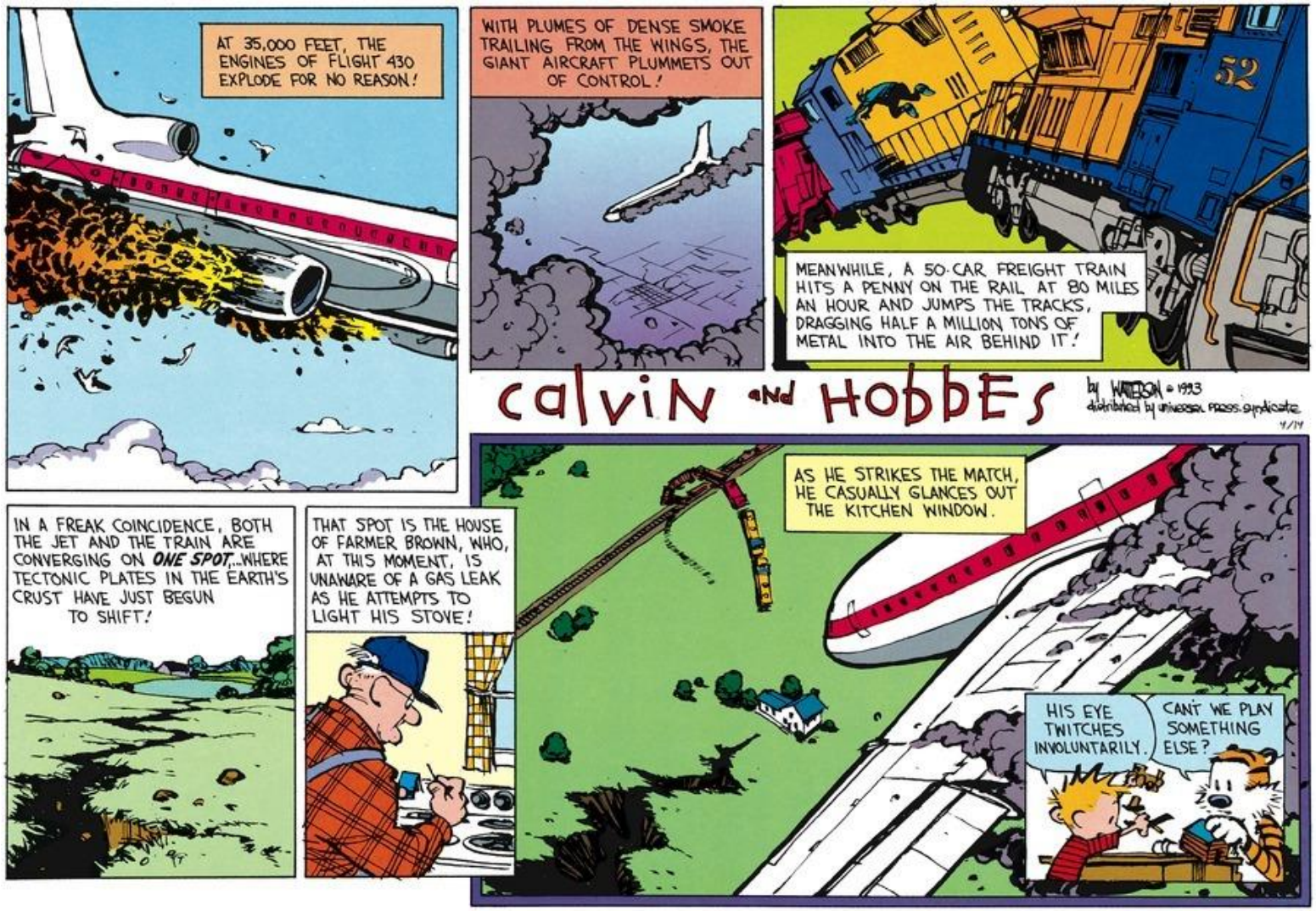
- Black Elephants[2]

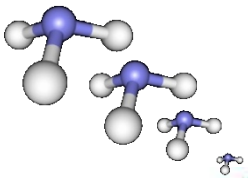


- Black Unicorns

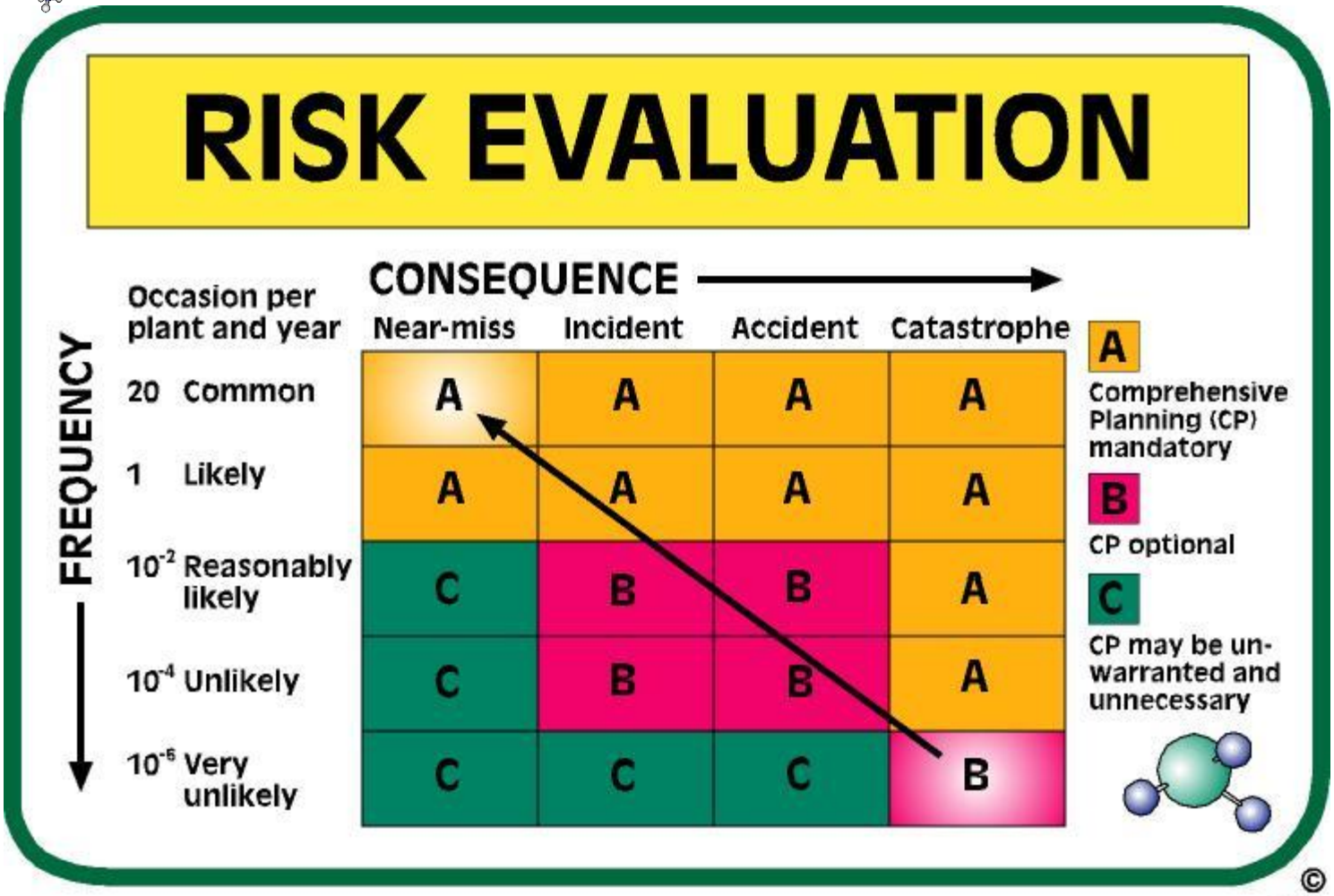
[1] Aven, T. (2015). Implications of black swans to the foundations and practice of risk assessment and management. *Reliability Engineering & System Safety*, *134*, 83-91.

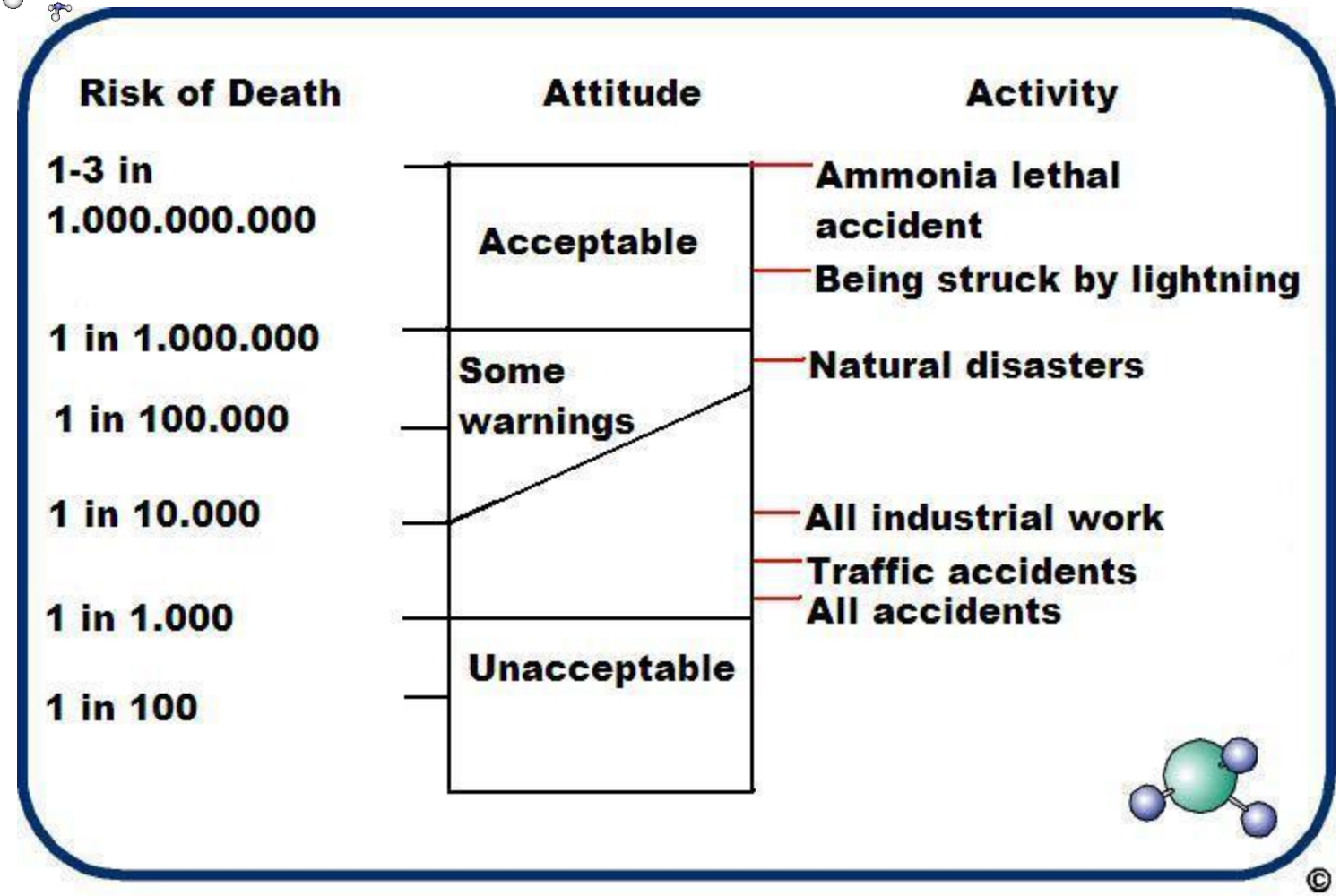
[2] Möller, N., & Wikman-Svahn, P. (2011). Black elephants and black swans of nuclear safety. Ethics, Policy & Environment, 14(3), 273-278.

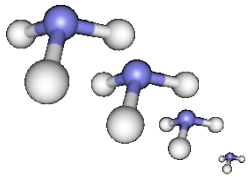

AT 35,000 FEET, THE ENGINES OF FLIGHT 430 EXPLODE FOR NO REASON!
WITH PLUMES OF DENSE SMOKE TRAILING FROM THE WINGS, THE GIANT AIRCRAFT PLUMMETS OUT OF CONTROL!
52
MEANWHILE, A 50-CAR FREIGHT TRAIN HITS A PENNY ON THE RAIL AT 80 MILES AN HOUR AND JUMPS THE TRACKS, DRAGGING HALF A MILLION TONS OF METAL INTO THE AIR BEHIND IT!
calvin and Hobbes
by WATTERSON © 1993
distributed by UNIVERSAL PRESS SYNDICATE
IN A FREAK COINCIDENCE, BOTH THE JET AND THE TRAIN ARE CONVERGING ON ONE SPOT...WHERE TECTONIC PLATES IN THE EARTH'S CRUST HAVE JUST BEGUN TO SHIFT!
THAT SPOT IS THE HOUSE OF FARMER BROWN, WHO, AT THIS MOMENT, IS UNAWARE OF A GAS LEAK AS HE ATTEMPTS TO LIGHT HIS STOVE!
AS HE STRIKES THE MATCH, HE CASUALLY GLANCES OUT THE KITCHEN WINDOW.
HIS EYE TWITCHES INVOLUNTARILY.
CAN'T WE PLAY SOMETHING ELSE?



RISK EVALUATION

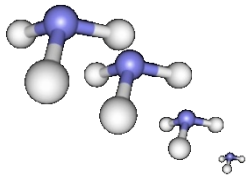



Risk of Death
Attitude
Activity
1-3 in 1.000.000.000
1 in 1.000.000
1 in 100.000
1 in 10.000
1 in 1.000
1 in 100
Acceptable
Some warnings
Unacceptable
Ammonia lethal accident
Being struck by lightning
Natural disasters
All industrial work
Traffic accidents
All accidents
©



Available facts about fatal accidents related to ammonia

- ***Number of fatalities is less than 2 persons per 1,000,000,000 (billion) population.***
- ***Such low figures do not normally justify extraordinacy regulatory measures.***
- ***Victims are those closest to a release, exposed to very high concentrations, and unable to escape or shelter-in-place.***
- ***Most fatalites are to workers, not responders or the public and are preventable.***

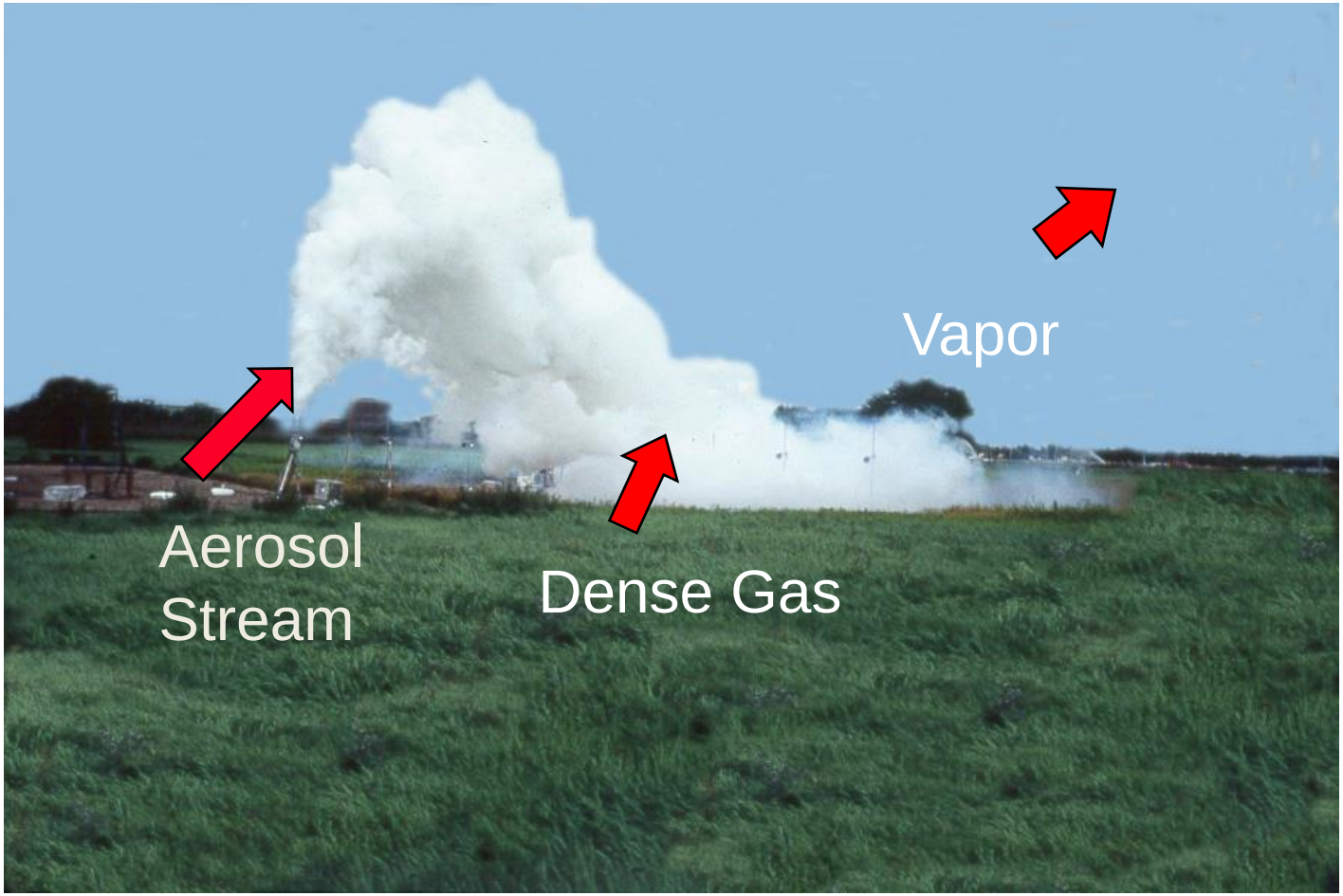


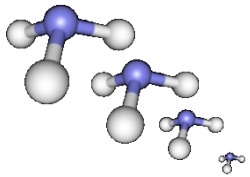
Threats

Control the Threats from:

- Fire
- Overpressure
- Release
- Reactivity
- Other (Natural, Terrorism, etc.)

Types of Release





Chemical Regulatory History

- Major Accidents
  - Flixboro (June 1974)
  - Seveso (July 1976)
  - Love Canal (1978)
  - Times Beach (1982)
  - Bhopal (December 1984)
  - West, TX (April 2014)
- Regulations
  - Occupational Safety
  - Environmental
  - Transportation
  - Chemical Safety/Risk Management
  - Homeland Security
- Codes and Standards

Terra Nitrogen

Sioux City, IA

- December 1994
- AN process explosion
- 5,700 Ton release
- 4 dead (not from NH3)

Photo 8 - 12
Water Tank Damage (Ammonia Tank Background)

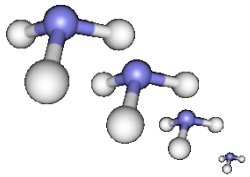
Photo 8 - 13
Ammonia Bullet Tank Damage

Explosion Cause Scenarios Page 80

Minot

Minot, ND

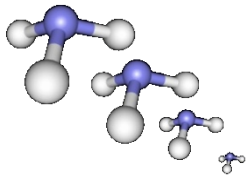
- January 2002
- Rail car derailment
- 5 tank cars ruptured
- 146,700 gal release
- 1 dead, 11 injuries
- 1 car travelled 1,200’
- +74,000 gal released over the next 6 days



Why You Shouldn't Believe Everything You Read On The Internet

Something important always gets left out.

Technion Ammonia Conference. November 2017



"Explosion Highlights Dangers of Anhydrous Ammonia"

The fire at a fertilizer plant in West, Texas killed between 5 and 15 people.

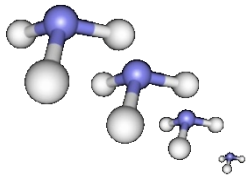
By **Ker Than**, for National Geographic News
PUBLISHED April 20, 2013

A fertilizer plant in the community of West, Texas that exploded on Wednesday to deadly effect was known to produce and store a volatile and potentially dangerous form of nitrogen-based fertilizer known as anhydrous ammonia.

Wednesday's explosion, which happened around 7:50 p.m., suggested otherwise. Beyond the death toll, which authorities said was unclear, **the blast injured dozens of people and was compared to a "nuclear bomb" by some witnesses.**

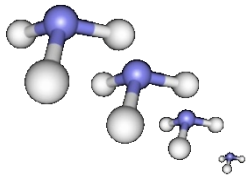
West Tx Fertilizer Plant
Explosion
April 17, 2013, 1953 hours

Technion Ammonia Conference. November 2017



LESSONS LEARNED
FROM AMMONIA RELEASES

Technion Ammonia Conference. November 2017



Ammonia accidents and incidents

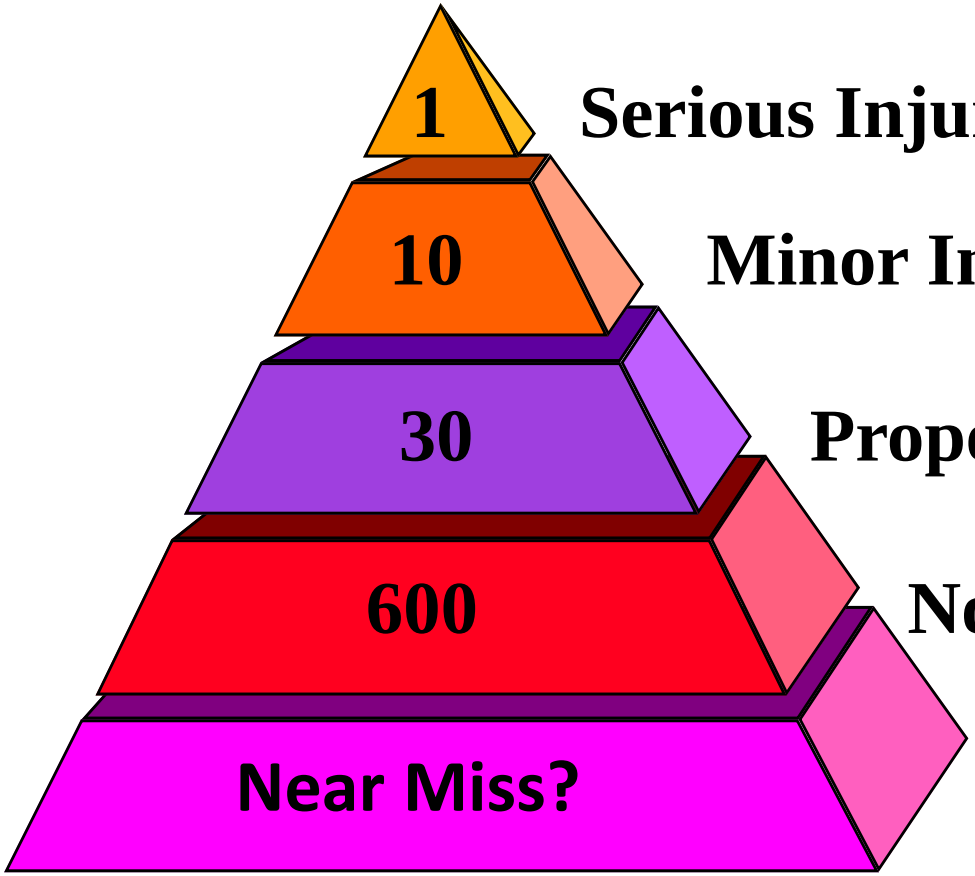
Ammonia releases are common.

Ammonia accidents that cause significant consequences (fatalities, injuries, property damage, off-site consequences, environmental damage, etc.), however, are rare.

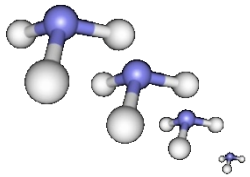
There are common/typical sources and causes of ammonia incidents.

Nearly all ammonia incidents can be prevented.

*Accident /Safety Triangle**



* *H. W. Heinrich, "Industrial Accident Prevention", 1931*
Frank E. Bird, Jr., "Practical Loss Control Leadership", 1985

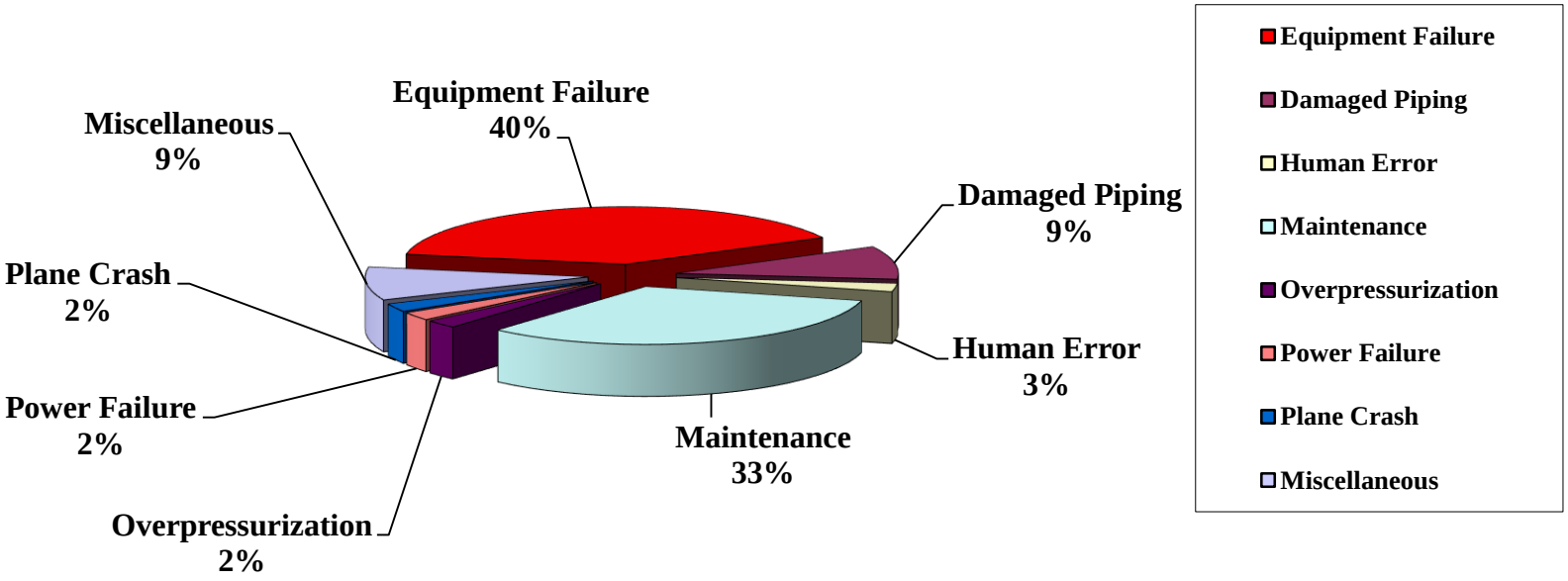


NH_3 Accident Research

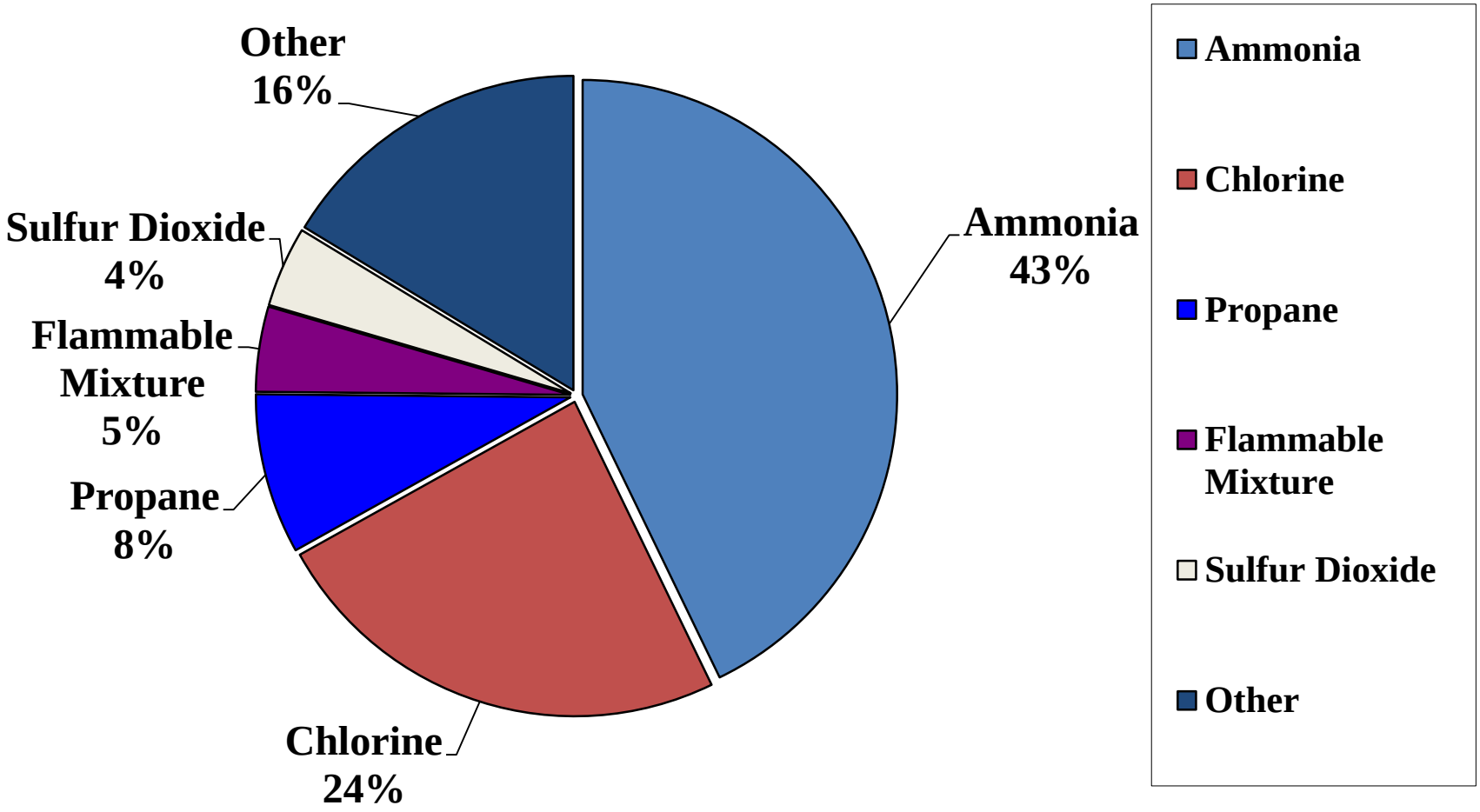
Collaboration with US Chemical Safety Board

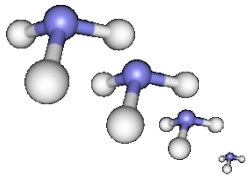
- HMIS database (US OSHA)
- RMP database (US EPA)
- Regulatory reporting (HSEES - CDC/HMIS -DOT)
- State regulatory search
- International
  - MARS (EU – Seveso Directive)
  - ARIA/BARPI (France)
  - HSE Accident Data (United Kingdom)

Ammonia Accident Causes - OSHA



RMP Database
Top 5 Chemicals





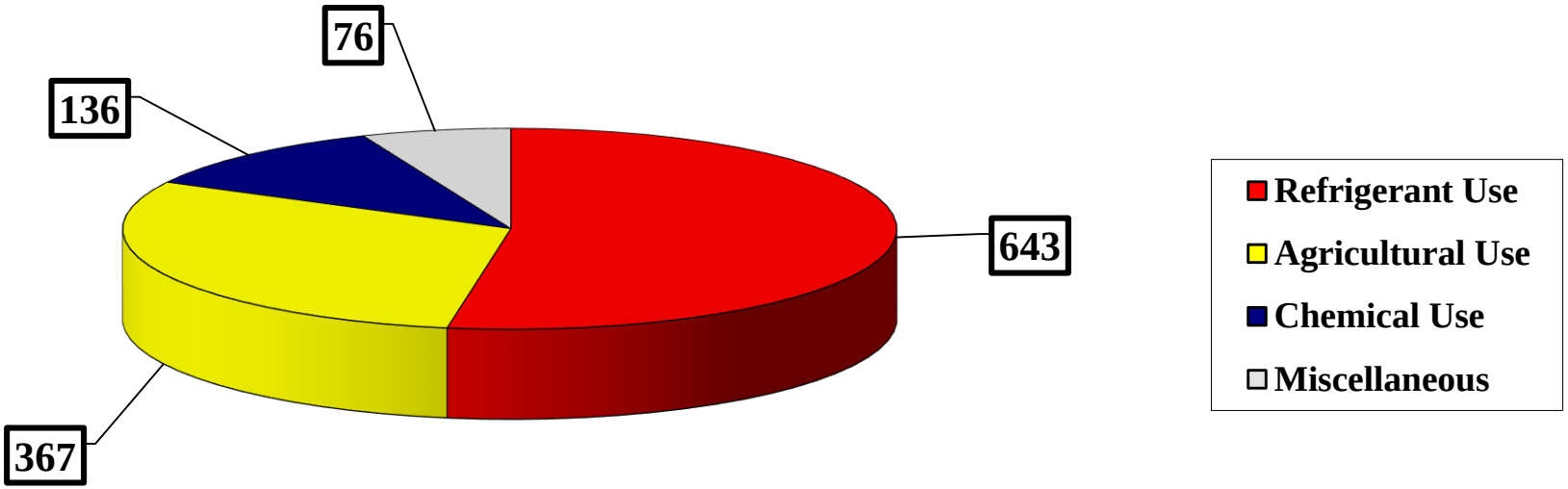
RMP Database 1994-2013

- **7,619 RMP covered facilities with reportable ammonia inventory**
- **Over 2,000 incidents involving ammonia (57%)**
- **Over 1,200 Ammonia refrigeration incidents**

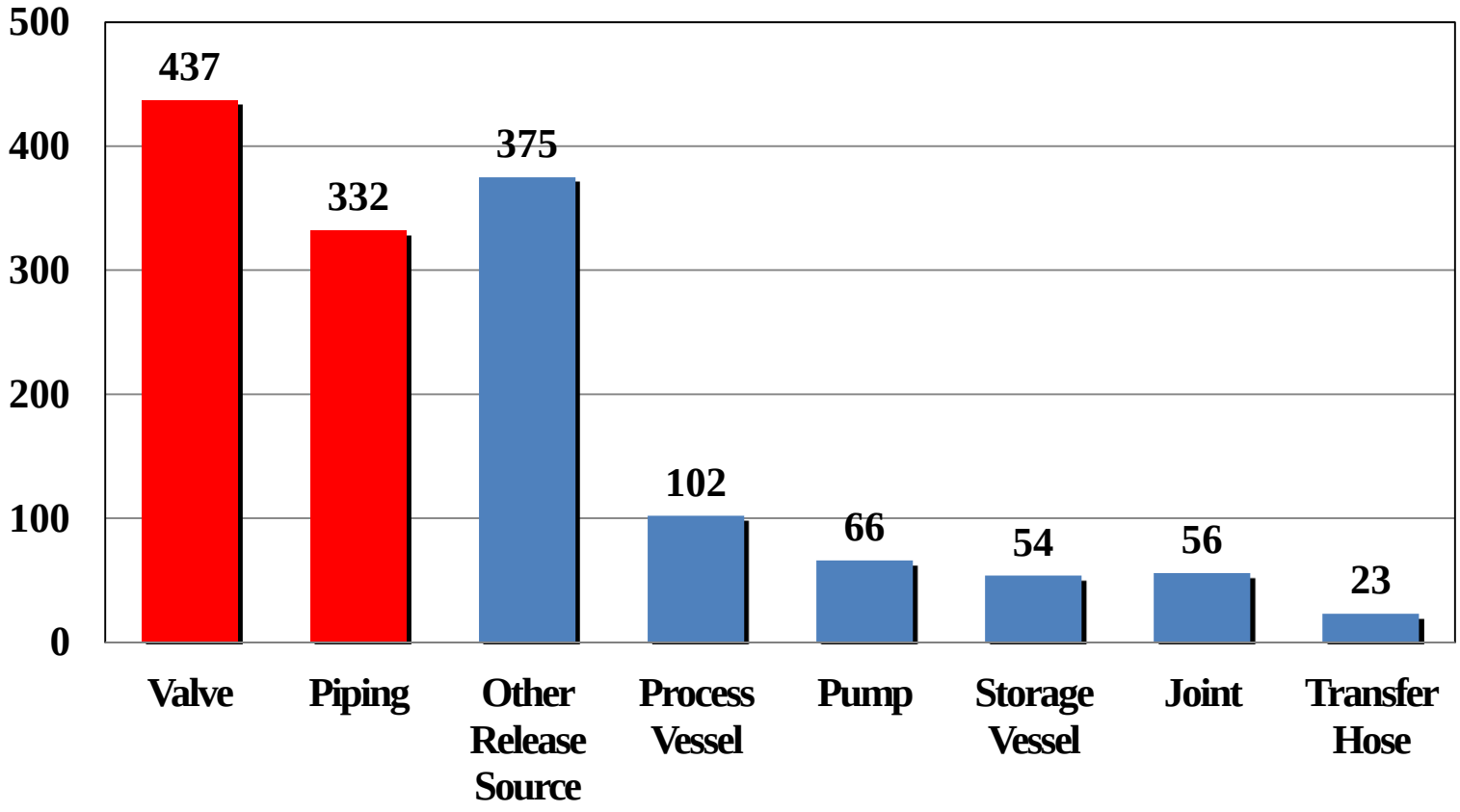
Ammonia is THE #1

- ✓ **RMP/PSM/CFATS Covered Chemical**
- ✓ **Chemical for RMP 5-year Accident History**

RMP Ammonia Incidents by Ammonia End Use 1994-2004

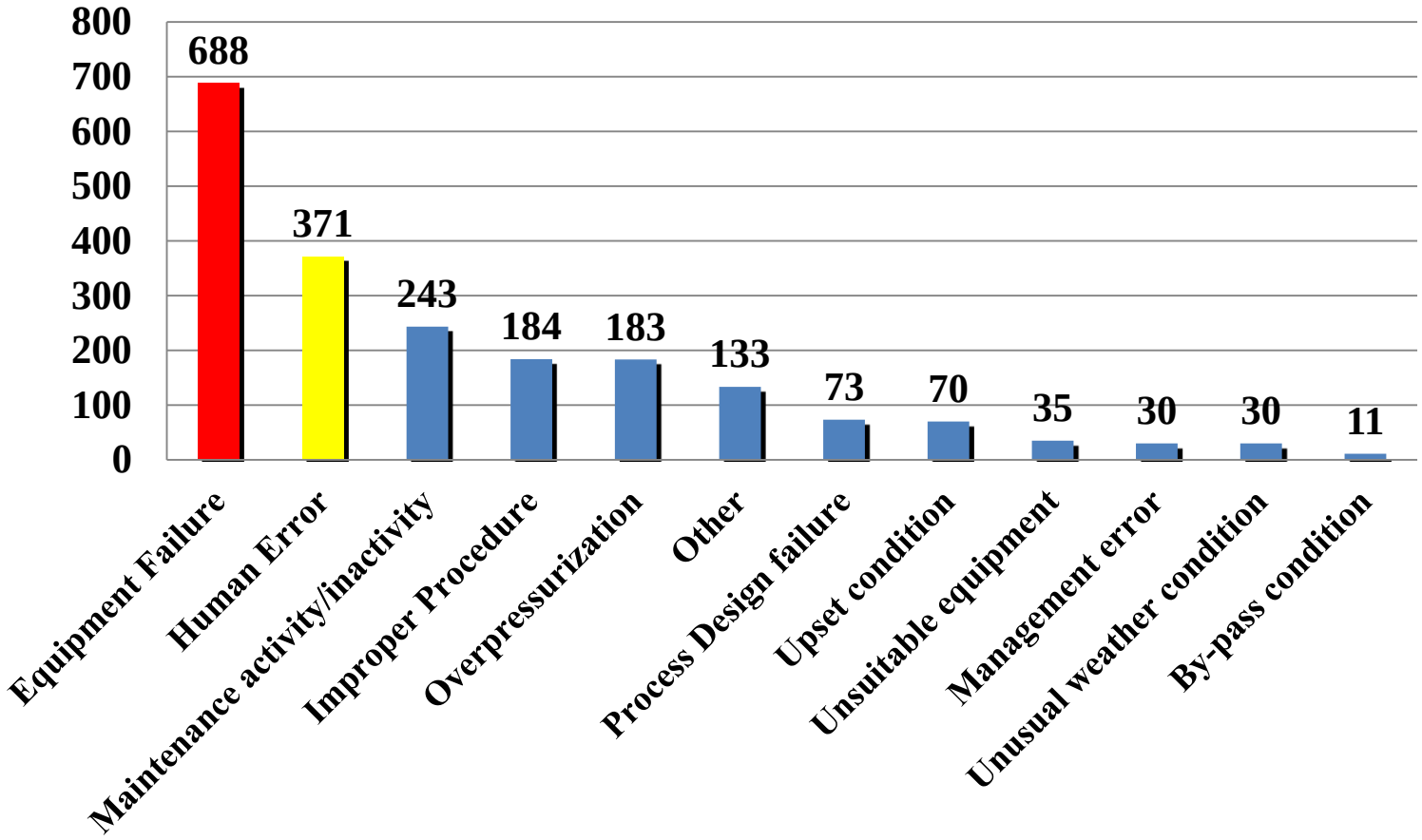


RMP Ammonia Incidents
Release Sources (1994-2013)



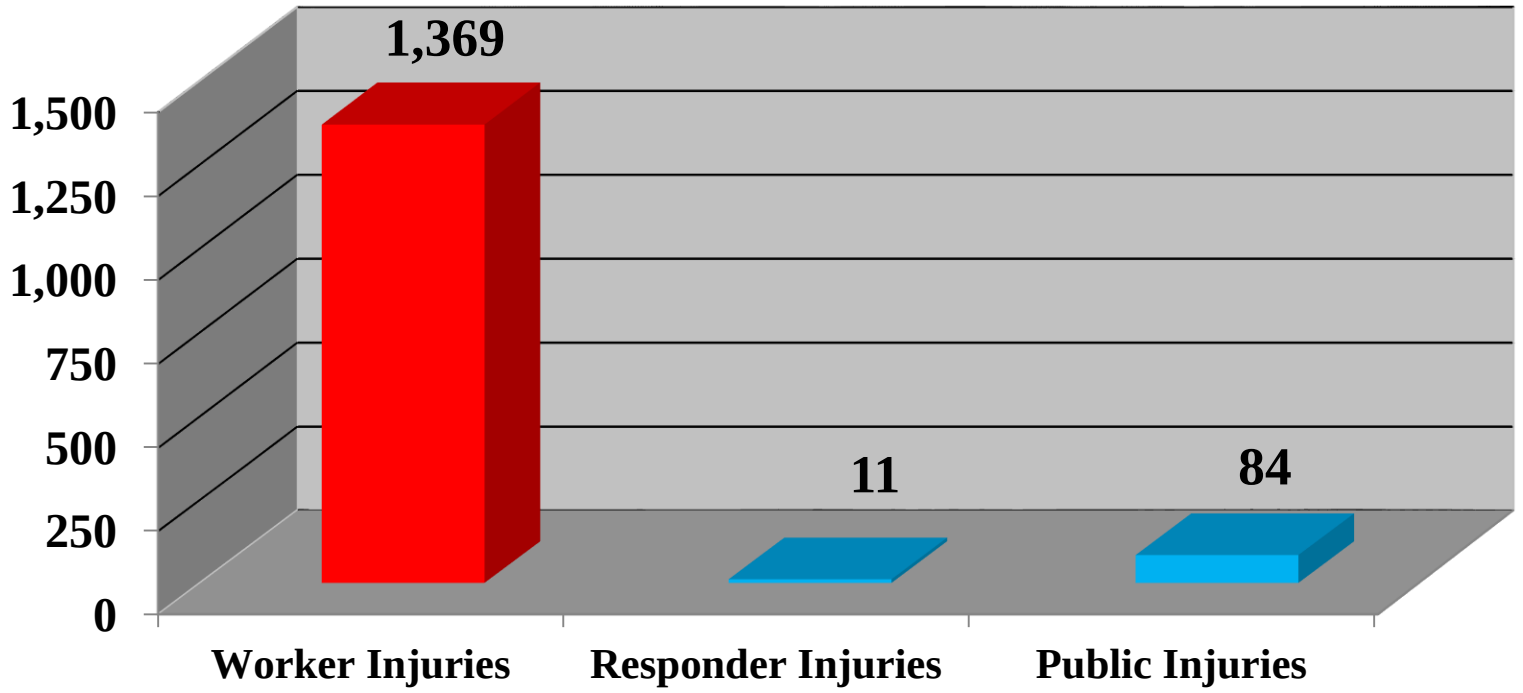
1,253 Total Releases

RMP Ammonia Incidents
Reasons for Release (1994-2013)

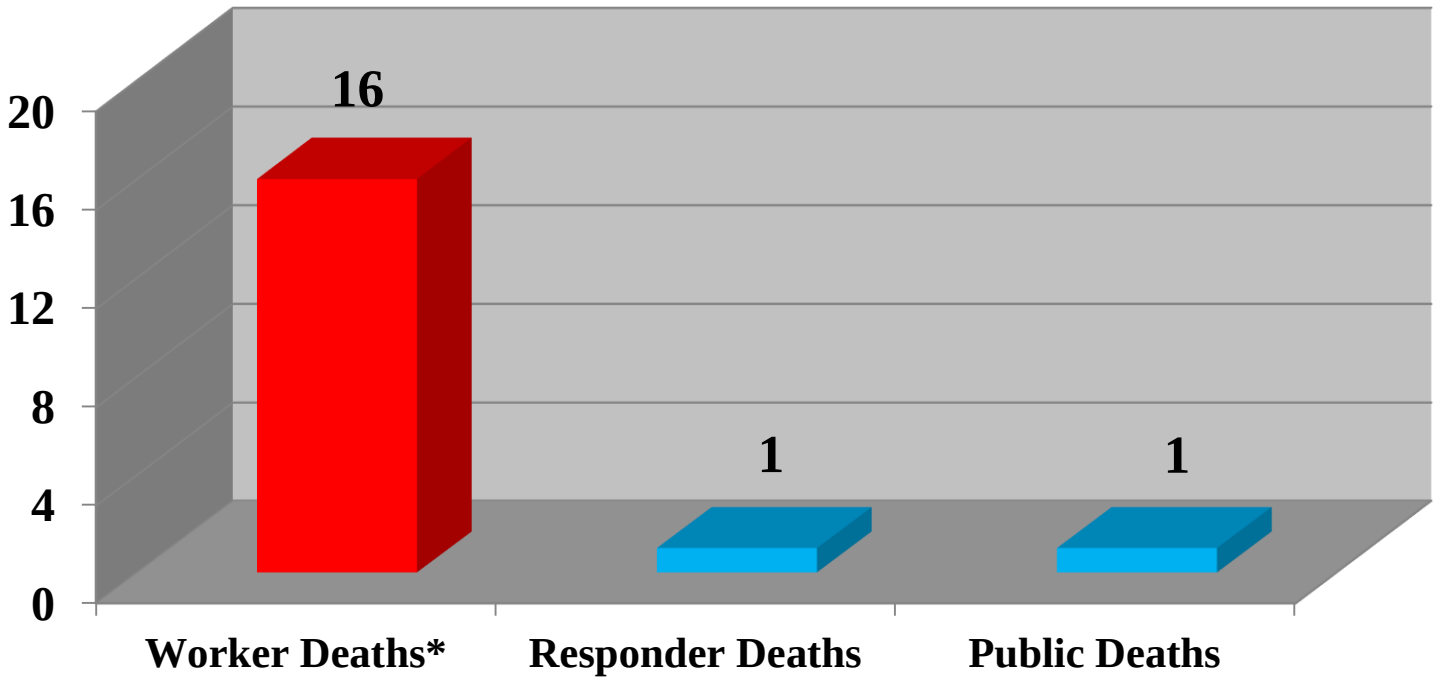


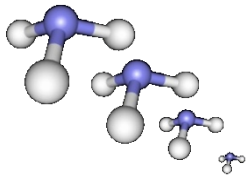
1,253 Total Releases

Ammonia
RMP Incident Injuries (1994-2013)



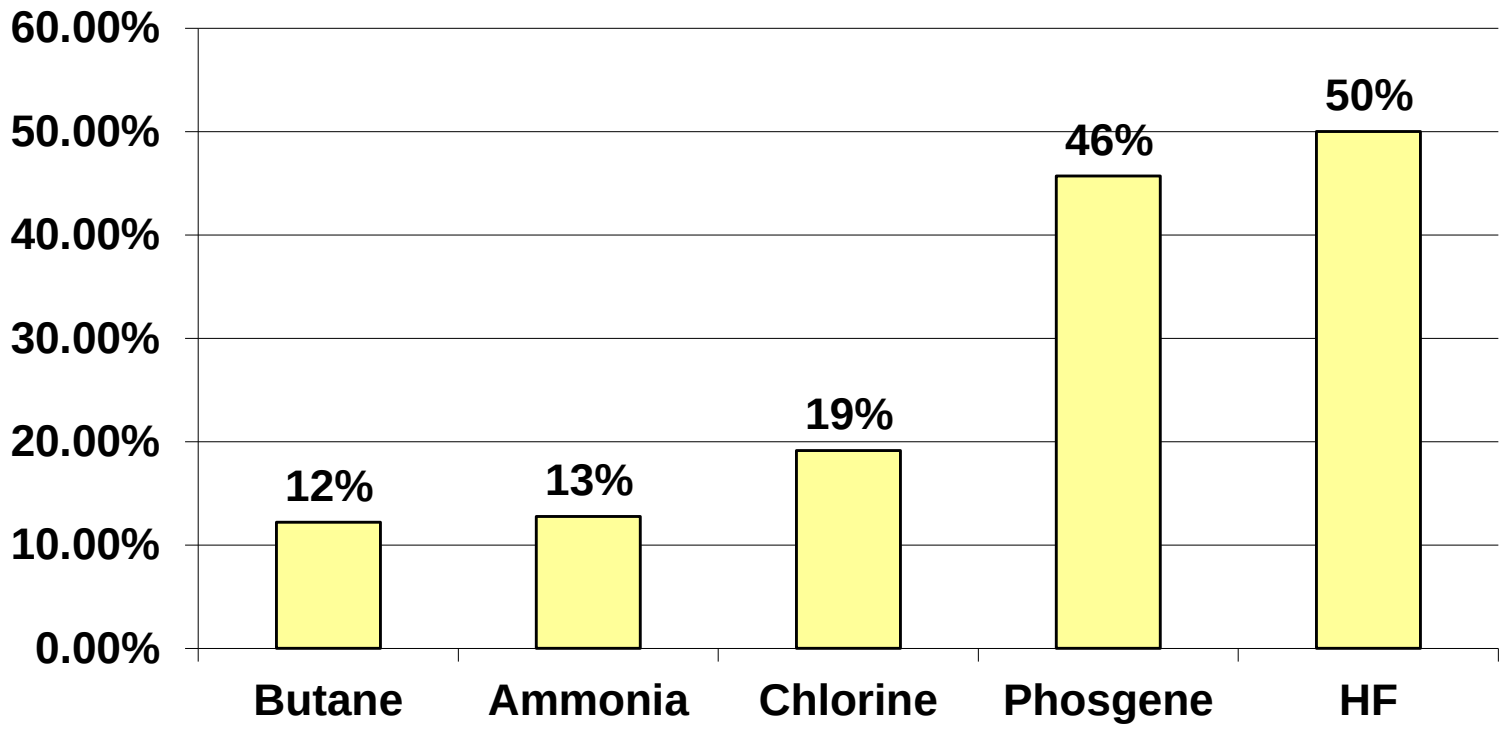
Ammonia
RMP Incident Fatalities (1994 – 2013)



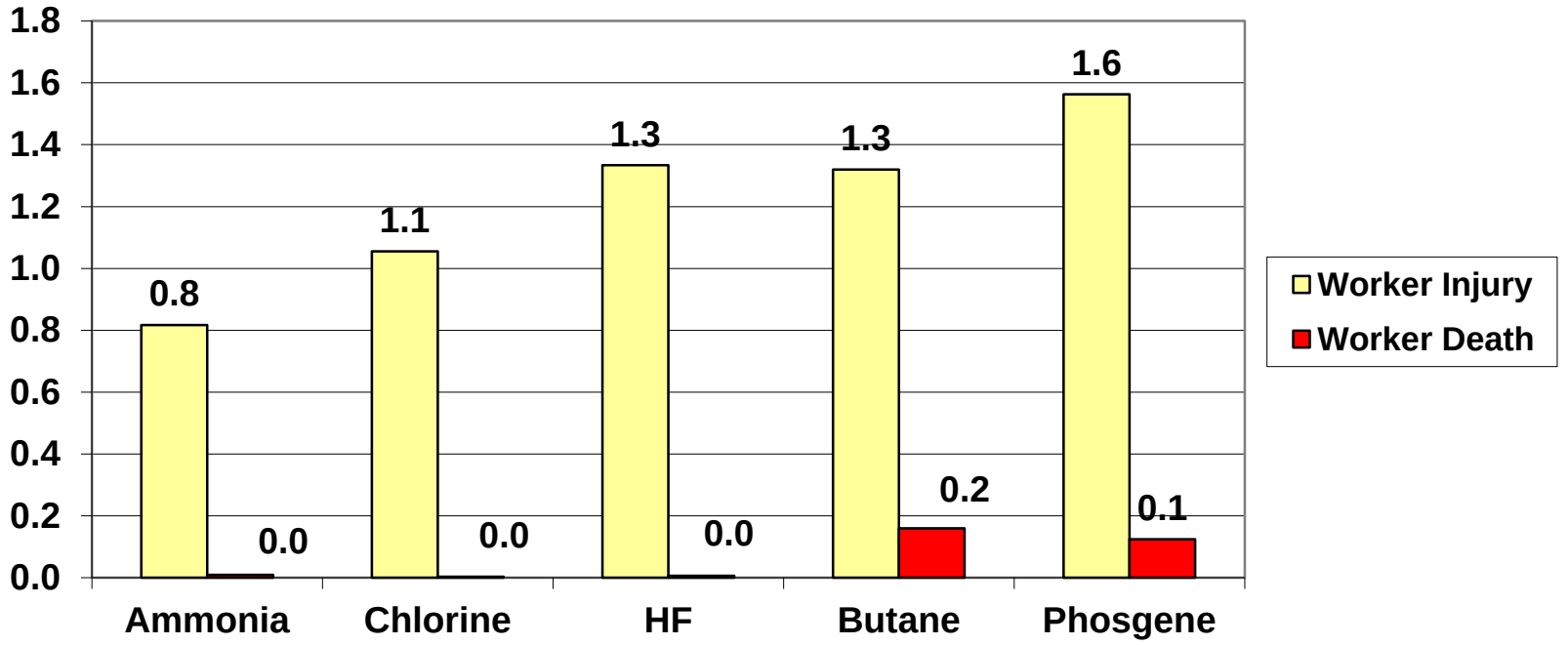


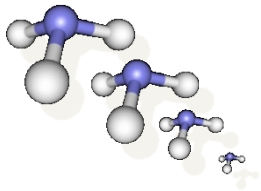
SOME COMPARISONS

RMP Incidents / Facility By Chemical



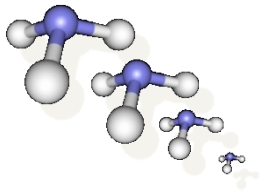
Average Injury/Fatality per Incident by Chemical





Conclusions

- Ammonia is one of the highest volume chemicals produced/used – in the top 5.
- Ammonia has been safely used for >150 years in tens of thousands of locations.
- Large, catastrophic accidental releases are rare and those that happened were preventable with safe design and good practices.
- The greatest risk of harm is to employees and workers exposed to high concentrations and closest to a release.



Conclusions – cont.

- Large volume storage and handling at low pressure is safer and less risk than pressurized storage.
- Assessments of risk and consequences must be credible, based on realistic assumptions and without overly conservative criteria.
- Ammonia is a chemical that deserves respect, but it should not be feared.