



Anhydrous Ammonia Emergency Response



24-hr Oil Spill Response/Cordova

10/5/2014

What do we hope to Learn

- Emergency response protocols/procedures
- Technical information about ammonia
- How does ammonia respond when release into an environment.
- The effects of weather on ammonia behavior
- When to use water to disperse ammonia vapor
- When is no approach the best approach

Ammonia Uses

- Industrial
 - Fertilizer production
 - Cleaning products
 - Chemical Industry
 - Pulp/Paper production
 - Explosives
 - Mining/Extraction
 - Refrigeration





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24-hr Oil Spill Response/Cordova

Emergency Response Priorities

- Life Safety is first priority
 - First Responders
 - Response based on training
 - Public
- Property
 - Outside (<LEL)</p>
 - Inside (LEL?)
- Environment
 - Water ways
 - Ground/soil
 - Drains



EMERGENCY RESPONSE GUIDEBOOK

A finishingk for First Responders Doring the formal Planie of a Dangerous Coordal (tamphone Materials Tramportation Inciden What Information about ammonia can we learn from the 2012 Emergency Response Guidebook?

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GUIDE GASES - CORROSIVE

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POTENTIAL HAZARDS

HEALTH

- · TOXIC; may be fatal if inhaled, ingested or absorbed through skin.
- · Vapors are extremely irritating and corrosive.
- · Contact with gas or liquefied gas may cause burns, severe injury and/or frostbite.
- · Fire will produce irritating, corrosive and/or toxic gases.
- · Runoff from fire control may cause pollution.

FIRE OR EXPLOSION

- · Some may burn but none ignite readily.
- · Vapors from liquefied gas are initially heavier than air and spread along ground.
- · Some of these materials may react violently with water.
- · Cylinders exposed to fire may vent and release toxic and/or corrosive gas through pressure relief devices.
- · Containers may explode when heated.
- · Ruptured cylinders may rocket.

PUBLIC SAFETY

- · CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.
- · As an immediate precautionary measure, isolate spill or leak area for at least 100 meters (330 feet) in all directions.
- · Keep unauthorized personnel away.
- · Stay upwind.
- · Many gases are heavier than air and will spread along ground and collect in low or confined areas (sewers, basements, tanks).

· Keep out of low areas.

· Ventilate closed spaces before entering.

PROTECTIVE CLOTHING

- · Wear positive pressure self-contained breathing apparatus (SCBA).
- · Wear chemical protective clothing that is specifically recommended by the manufacturer. It may provide little or no thermal protection.
- · Structural firefighters' protective clothing provides limited protection in fire situations ONLY; it is not effective in spill situations where direct contact with the substance is possible.

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EVACUATION

Spill

See Table 1 - Initial Isolation and Protective Action Distances for highlighted materials. For non-highlighted materials, increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".

Fire

· If tank, rail car or tank truck is involved in a fire, ISOLATE for 1600 meters (1 mile) in all directions; also, consider initial evacuation for 1600 meters (1 mile) in all directions.

EMERGENCY RESPONSE

Fire

Small Fire

· Dry chemical or CO2.

Large Fire

- · Water spray, fog or regular foam.
- · Move containers from fire area if you can do it without risk.
- · Do not get water inside containers.
- · Damaged cylinders should be handled only by specialists.

Fire involving Tanks

- · Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
- · Cool containers with flooding quantities of water until well after fire is out.
- · Do not direct water at source of leak or safety devices; icing may occur.
- · Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- · ALWAYS stay away from tanks engulfed in fire.

SPILL OR LEAK

- · Fully encapsulating, vapor protective clothing should be worn for spills and leaks with no fire.
- · Do not touch or walk through spilled material.
- · Stop leak if you can do it without risk.
- · If possible, turn leaking containers so that gas escapes rather than liquid.
- · Prevent entry into waterways, sewers, basements or confined areas.
- · Do not direct water at spill or source of leak.
- · Use water spray to reduce vapors or divert vapor cloud drift. Avoid allowing water runoff to contact spilled material.

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- · If possible, turn leaking containers so that gas escapes rather than liquid.
- · Prevent entry into waterways, sewers, basements or confined areas.
- · Do not direct water at spill or source of leak.
- · Use water spray to reduce vapors or divert vapor cloud drift. Avoid allowing water runoff to contact spilled material.
- · Isolate area until gas has dispersed.

FIRST AID

- · Move victim to fresh air.
- · Call 911 or emergency medical service.
- · Give artificial respiration if victim is not breathing.
- Do not use mouth-to-mouth method if victim ingested or inhaled the substance; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.
- · Administer oxygen if breathing is difficult.
- · Remove and isolate contaminated clothing and shoes.
- · In case of contact with liquefied gas, thaw frosted parts with lukewarm water.
- · In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes.
- In case of contact with Hydrogen fluoride, anhydrous (UN1052), flush skin and eyes with water for 5 minutes; then, for skin exposures rub on a calcium/gel combination; for eyes flush with a water/calcium solution for 15 minutes.
- · Keep victim warm and quiet.
- · Keep victim under observation.
- · Effects of contact or inhalation may be delayed.
- · Ensure that medical personnel are aware of the material(s) involved and take precautions to protect themselves.

Technical Specifications

- Colorless, liquefied compressed gas
- Converts to a vapor when released
- Pungent, suffocating odor
- Odor Threshold: 2 45 ppm
- Generally, not flammable (range in air must be 15 28%)
- Readily reacts w/ acids/halogens can be oxidized or reduced

Technical Specifications

- Anhydrous without Water
 Ammonia loves water
- Aqueous Solution- 19-35% solution
- Refrigerant mixed with oil
- 5 lbs./Gallon
- Pressure directly proportional to temperature
- High Coefficient of expansion (800 to 1)

Tactical Priorities

- Secure and deny entry use ERG initially
- Size-up/access the situation
- Request additional resources as needed
- Protect target receptors
 - Evacuate or Shelter-in-place
- Minimize the effects of ammonia (chemical)
- Control the spread of Ammonia (chemical)
- Stop the release if it can be done safely with minimum risk to hazmat technician first responders







What does the NIOSH Pocket Guide have to tell us about Ammonia?

DEPARTMENT OF HEALTH AND HUMAN SERVICES Centers for Disease Control and Prevention National Institute for Occupational Safety and Health

10/5/2014

Ammonia

Synonyms & Trade Names Anhydrous ammonia, Aqua ammonia, Aqueous ammonia [Note: Often used in an aqueous solution.]

| CAS No. 7664-41-7 | RTECS No. <u>B00875000</u> | DOT ID & Guide 1005 <u>125</u> ଜି (anhydrous) 2672 <u>154</u> ଜି(10-35% solution) 2073 <u>125</u> ଜି(>35-50% solution) 1005 <u>125</u> ଜି(>50% solution) | |
|---|---|--|--|
| Formula NH ₃ | Conversion 1 ppm = 0.70 mg/m ³ | IDLH 300 ppm See: <u>7664417</u> | |
| Exposure Limits NIOSH REL : TWA 25 ppm (18 mg/m ³) ST 35 ppm (27 mg/m ³) OSHA PEL <u>†</u> : TWA 50 ppm (35 mg/m ³) | | Measurement Methods NIOSH <u>3800</u> 觉, <u>6015</u> 한, <u>6016</u> 한; OSHA ID188 & See: <u>NMAM</u> or <u>OSHA Methods</u> & | |

Physical Description Colorless gas with a pungent, suffocating odor. [Note: Shipped as a liquefied compressed gas. Easily liquefied under pressure.]

| MW: 17.0 | BP: -28°F | FRZ: -108°F | Sol: 34% | VP: 8.5 atm | IP: 10.18 eV |
|-------------|-------------------|-------------|----------|-------------|---------------------|
| | FI.P: NA (Gas) | UEL: 28% | LEL: 15% | RGasD: 0.60 | |

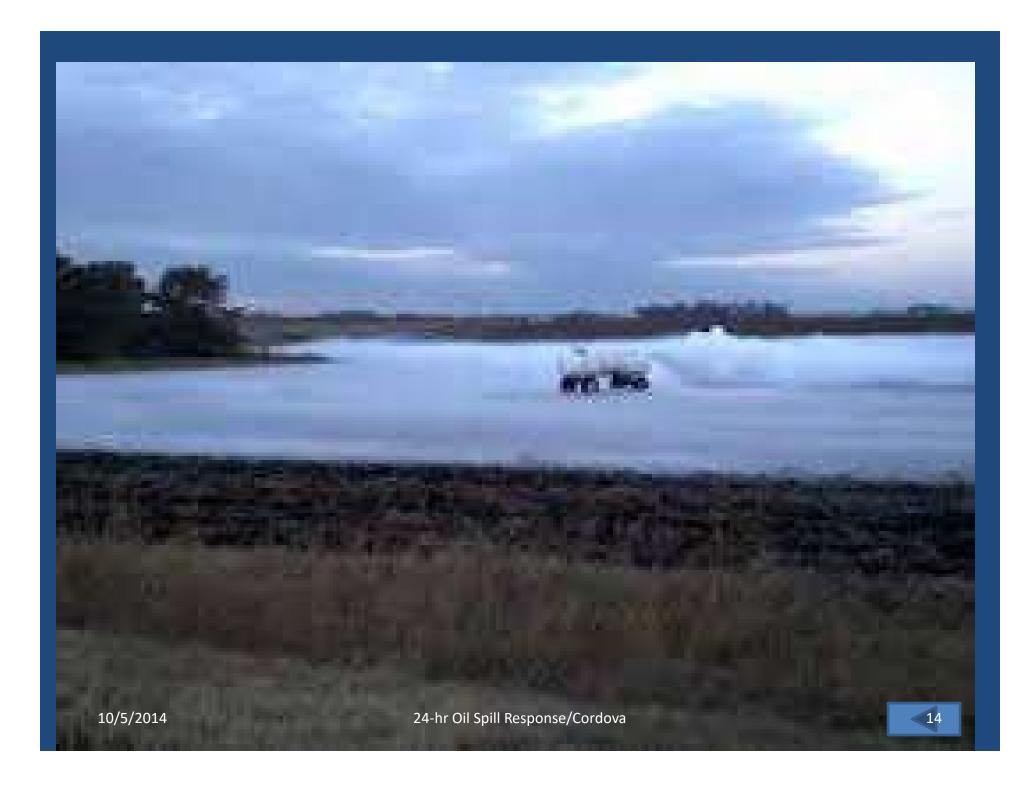
[Note: Although NH_3 does not meet the DOT definition of a Flammable Gas (for labeling purposes), it should be treated as one.]

Incompatibilities & Reactivities Strong oxidizers, acids, halogens, salts of silver & zinc [Note: Corrosive to copper & galvanized surfaces.]

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Exposure Routes inhalation, ingestion (solution), skin and/or eye contact (solution/liquid)

Symptoms irritation eves, nose, throat: dyspnea (breathing difficulty), wheezing, chest pain:



Flammable Range



Concentration of vapor in air

| Chemical | Flash Point | LEL | UEL | |
|------------------------|--------------------|------|------|--|
| Gasoline | -45 [°] F | 1.4% | 7.6% | |
| Anhydrous Ammonia | None | 15% | 28% | |
| Ammonia Refrigerant | NA | 6% | 8% + | |

Exposure Routes inhalation, ingestion (solution), skin and/or eye contact (solution/liquid)

Symptoms irritation eyes, nose, throat; dyspnea (breathing difficulty), wheezing, chest pain; pulmonary edema; pink frothy sputum; skin burns, vesiculation; liquid: frostbite

Target Organs Eyes, skin, respiratory system

| Personal Protection/Sanitation (See protection | First Aid (See procedures) |
|--|--------------------------------|
| codes) | Eye: Irrigate immediately |
| Skin: Prevent skin contact | (solution/liquid) |
| Eyes: Prevent eye contact | Skin: Water flush immediately |
| Wash skin: When contaminated (solution) | (solution/liquid) |
| Remove: When wet or contaminated (solution) | Breathing: Respiratory support |
| Change: No recommendation | Swallow: Medical attention |
| Provide: Eyewash (>10%), Quick drench (>10%) | immediately (solution) |

Respirator Recommendations

NIOSH

Up to 250 ppm:

(APF = 10) Any chemical cartridge respirator with cartridge(s) providing protection against the compound of concern*

(APF = 10) Any supplied-air respirator*

Up to 300 ppm:

(APF = 25) Any supplied-air respirator operated in a continuous-flow mode*

(APF = 25) Any powered, air-purifying respirator with cartridge(s) providing protection against the compound of concern*

(APF = 50) Any chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against the compound of concern

(APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against the compound of concern

(APF = 50) Any self-contained breathing apparatus with a full facepiece

(APF = 50) Any supplied-air respirator with a full facepiece

Emergency or planned entry into unknown concentrations or IDLH conditions:

(APF = 10,000) Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode

Up to 300 ppm:

(APF = 25) Any supplied-air respirator operated in a continuous-flow mode*

(APF = 25) Any powered, air-purifying respirator with cartridge(s) providing protection against the compound of concern*

(APF = 50) Any chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against the compound of concern

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(APF = 10,000) Any supplied-air respirator that has a full facepiece and is operated in a pressure demand or other positive-pressure mode in combination with an auxiliary self-contained positivepressure breathing apparatus

Escape:

(APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against the compound of concern Any appropriate escape-type, self-contained breathing apparatus

Important additional information about respirator selection

Technical Specifications

Domestic DOT Group: 2.2 (Poison Gas) –
 1005

24-hr Oil Spill Response/Cordova

- International Groups 2.3 & 8
- NFPA Class: 3/1/0
- SG: 0.6
- Vapor/Liquid Volume Ratio: 800:1
- BP: 28.1 F
- IP: 10.18 eV



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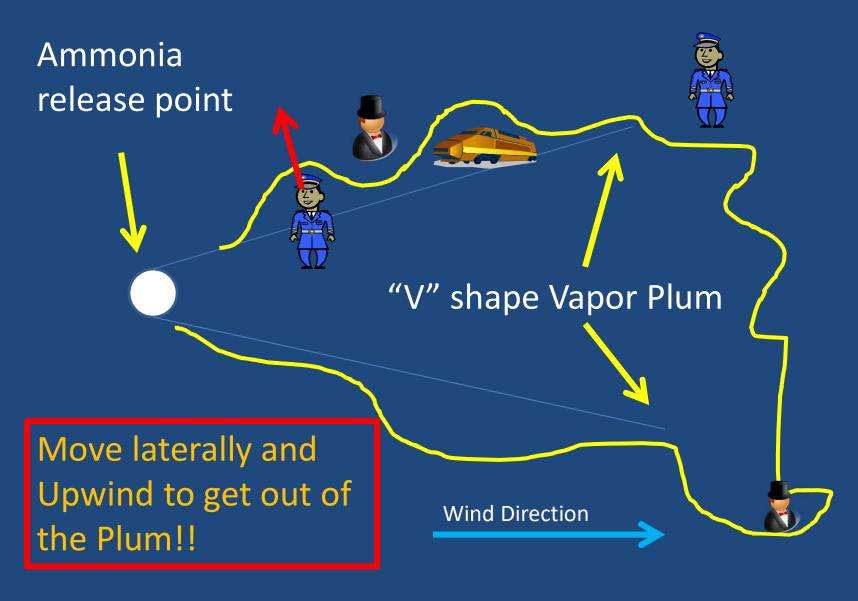
Anatomy of an Ammonia Cloud

AerosolDenseStreamGas/Vapor

Vapor or Trace Gas

Horseshoe Effect

Anatomy of an Ammonia Cloud



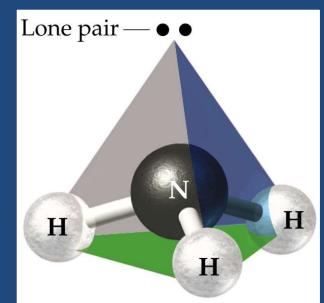
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What does weather do to an Ammonia Plum?

- Wind dilutes and spreads the plum
- Temperature Effects pressures
 - Cold Holds plum down
 - Hot Moves plum up and away
- Humidity Moistures holds ammonia

Chemistry

- Ammonia consists of nitrogen with three hydrogens and a lone pair
- Nitrogen's lone pair is readily able to react
- Oxidation States: -3, -2, -1/3, 1, 2, 3, 4, 5
- Many compounds can be generated:
 - Ammonium
 - Hydrazine
 - Azides
 - NOx
 - Nitrites
 - Nitric Acid/Nitrates



Health and Safety

- Exposure limits:
 - PEL-TWA: 50 ppm (35 mg/m³)
 - REL/TLV-TWA: 25 ppm (18 mg/m³)
 - STEL/TLV Ceiling: 35 ppm (27 mg/m³)
 - IDLH: 300 ppm
 - Fatal Dose: 5,000 ppm for 5 mins
- Responder guidelines require APRs <= 250 ppm

SCBAs w/ Level A/B => 250 – 300 ppm

Health and Safety

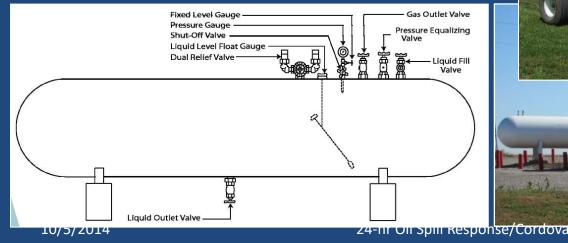
- Exposure Symptoms
 - Eye/nose/throat irritation
 - Skin burns/frostbite (liquid)
 - Respiratory distress including wheezing/pain
- Treatment of Exposure
 - Flush eyes/skin for 15+ mins and treat affected skin as a thermal burn
 - Provide fresh air or artificial respiration

• AEGLs

| ppm (mg/m³) | 10 min | 30 min | 1 hr. | 4 hr. | 8 hr. |
|-----------------|---------|---------|-------|-------|-------|
| AEGL-1 | 30 | 30 | 30 | 30 | 30 |
| (non-disabling) | (21) | (21) | (21) | (21) | (21) |
| AEGL-2 | 220 | 220 | 160 | 110 | 110 |
| (disabling) | (154) | (154) | (112) | (77) | (77) |
| AEGL-3 | 2,700 | 1,600 | 1,100 | 550 | 390 |
| (lethal) | (1,888) | (1,119) | (769) | (385) | (273) |

Ammonia Storage

- Cylinders
 - Typical Sizes: 15, 50, 65, 100, 150 (lbs.)
 - CGA Valves 240 and 705
- Nurse Tanks
- Bulk Storage





Ammonia Transport

- Truck
 - 9000-gal
- Rail
 - 35,000-gal
- Barge
 100,000-gals
- Vessel Storage
 100-1000-gal level



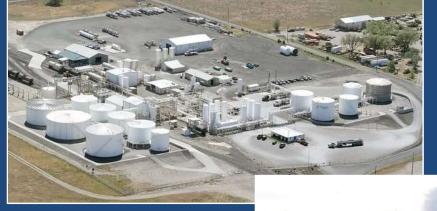


Response Scenarios

- Fixed Facilities
 - Producers/Users
 - Terminal/Storage
- Orphan Cylinders
- Transportation Incidents
 - Trawlers/Barges
 - Trucks/Trains







Site Characterization

- Plume Modeling
 - ALOHA
 - Cameo
- Air Monitoring
 - RAEs: NH3 sensor to 50-100 ppm (PID to 2,000)
 - PAC 7000s: 300 ppm (requires 12hr warm-up)
 A1 = 35 ppm; A2 = 250 ppm
- Sampling
 - SKC: Sorbent Tubes (226-61/226-29)
 - NMAM 6015/OSHA 188
- Source Threat Mitigation
 - ER Kits

Case Study

- Pacific Producer (WCY8623) Aug 2012
 - Leak began after RP performed repairs to an onboard freezer docked at Fisherman's Terminal
 - Liquid ammonia was discharged to ship containment below deck
 - SFD attempted to stop the leak but suffered exposures due to improper PPE and precautions
 - START monitored ammonia vapors and SFD/USCG activities



March 15, 2013



Case Study

- Dari gold July 2012
 - Leak in dairy tank cooling lines released ~4000 lbs. of liquefied ammonia
 - SFD evacuated/sheltered in place surrounding public and made entry to the facility
 - EPA/START deployed AreaRAEs downwind to monitor potential exposure to public
 - An AreaRAE with PID was provided to SFD to assess levels in the facility (exceeded 100 ppm and poisoned PID)



Questions

