Section 4: Anhydrous Ammonia Response

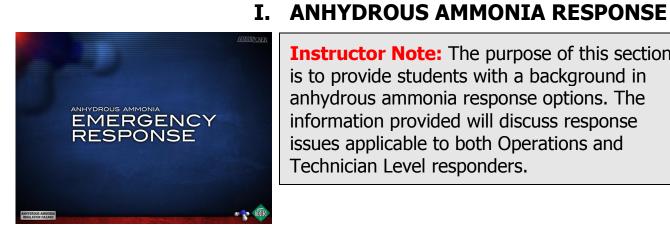
Lesson Goal

After completing this lesson, the student should be familiar with response to anhydrous ammonia events

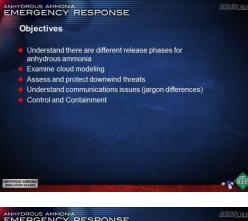
Objectives

Upon successful completion of this section, the student should be able to:

- A. Understand the potential release phases that can be encountered when dealing with an anhydrous ammonia release
- B. Understand real life cloud modeling and weather impacts on ammonia releases and release phases
- C. Employ safety measures such as assessing and protecting downwind threats.
- D. Understand terms and jargon used during an anhydrous ammonia emergency and how they may affect communication during the event
- E. Implement basic control and containment options for anhydrous ammonia



Instructor Note: The purpose of this section is to provide students with a background in anhydrous ammonia response options. The information provided will discuss response issues applicable to both Operations and







OSHA Response Levels Α.

Technician Level responders.

- First Responder Operations 1.
 - Those responders who would a. respond to a hazardous materials release as part of the initial response
 - b. Those trained to use defensive actions to contain the release from a safe distance, and keep it from spreading and prevent exposures
- First Responder Technician 2.
 - Those individuals who а. respond to the release for the purpose of stopping the release





- b. They will approach the point of release to plug, patch, or otherwise stop the release of a hazardous substance
- 3. We will discuss issues that are applicable to both Operations and Technician level responders
- Note for the students the difference between Operations and Technician level response approaches
- 5. We will discuss control and containment options for both levels of responders
- 6. Emergency Contact Numbers

B. Global Issues in Ammonia Release

- 1. Release Phases
 - a. Vapor
 - i. Ammonia exists naturally as an invisible vapor
 - When contained in a vessel the pressure and temperature of the ammonia determines the strength of the release

- A dense gas phase is created when the liquid inside a container escapes: the ammonia liquid is now boiling, changing from a liquid phase to vapor phase to create the aerosol and dense gas cloud
- c. Aerosol
 - i. The liquid escapes as an aerosol and then mixes with the atmosphere to create a dense gas cloud
 - ii. For the most part this could be condensation of humidity in the air which forms the white cloud
 - iii. It then escapes to the atmosphere as an invisible vapor
 - iv. At times the escaping aerosol can be contained with a tarp or other cover and the aerosol will condense into a liquid
- d. Liquid
 - i. Pressure within a vessel holds ammonia as a liquid

- ii. Liquids may exist when large volumes of the liquid are suddenly released from the vessel
- Once the pressure is released the liquid will flash off until a puddle of liquid remains and slowly evaporates to the atmosphere
- 2. Weather Impact
 - a. Wind
 - i. The most powerful mover of ammonia
 - ii. High wind will stream out the release
 - Moderate wind will maximize dispersion especially if the upper air is warm
 - b. Rain/Humidity
 - i. Ammonia loves water
 - ii. Ammonia will become a heavier than air gas cloud when mixed with water vapor
 - c. Temperature
 - i. Cold temps slows the cloud dispersion
 - ii. Warm temps adds energy to the ammonia molecule thus helping it spread more rapidly

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Release Phases

 • Vapor or Trace Gas

 • Dense gas

 • Aerosol

 • Liquid

 * Stream

 • Dense Gas

 • Stream

 • Dense Gas

EMERGENCY RESPONSE

- iii. Thermodynamic Rule: Warm always moves to cool so ammonia clouds will hang in lower, cooler and more moist areas
- 3. Environmental Impacts
 - a. Run off should be controlled
 - b. Keep out of drains and waterways
- 4. Terminology Differences
 - a. Industry
 - b. Public Sector

C. Release Phases

- 1. There are four release phases- this picture shows three of them: aerosol, dense gas and vapor
- 2. Aerosol Phase
 - a. Aerosol is converted to a sub-cooled gas that saturates the air and rides a buoyant gas cloud
 - b. Distances vary depending on:
 - i. Wind dispersion
 - ii. Weather conditions
 - iii. Amount of the release
 - iv. Distance of the aerosol stream



- c. A high pressure/high volume release during a humid and or cold day can develop dense gas clouds that remain close to the ground
- 3. Vapor Phase
 - a. Ammonia escapes the aerosol and dense gas as the heated air moves to warm the releases
 - b. The time for vaporization is dependent on the temperature of the air and humidity
 - c. Dry and warm days provide the quickest dissipation of ammonia aerosol and dense gas to vapor
- 4. Liquid Phase
 - a. Ammonia liquid occurs when the surrounding atmosphere and containment area are cooled to at least -28 F
 - b. Ammonia liquid is fairly stable when left to slowly boil off
 - c. If heat and water is added or the ammonia is spread on the ground it will produce boiling evaporation
- 5. Three risk factors from leaks
 - a. Life: yours and the public's
 - b. Environment: Downstream pollution concerns

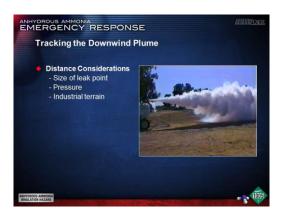


- c. Product/Facility: Chemical inventory and equipment exposure and corrosion challenges
- d. Wet weather, cold weather or a water or moisture source can keep the cloud close to the ground

D. Liquid Anhydrous Ammonia Considerations

- 1. Low pressure liquid is relatively safe if contained
- 2. After vaporizing and absorbing the surrounding heat, the liquid settles into a "sleeping" state
- 3. When the liquid is allowed to escape and react with the heat and moisture of the surroundings it will vaporize and boil off again
- Ammonia loves water and will search it out in the environment. Ammonia's attraction to water is stronger than the attraction to air.
- One volume of water will absorb 1300 volumes of ammonia vapor. The expansion ratio of ammonia is 840 to 1.
- 6. When released from containment, ammonia boils and makes a "frying egg" sound. Those that have experienced this have said that it sounded and felt like frying eggs on their face





7. Thus the need for the proper personal protective equipment

E. Tracking the Downwind Release

- 1. Chemical and physical characteristics of an outside release are dependent on volume pressure
- 2. Higher temps bring higher and more active pressure and vapor movement
- 3. Humidity and extremely cold temps slows vaporization
- 4. Ammonia is a cool gas and will track along valleys where temps are cooler
- 5. Plant life, ponds, rivers etc. will draw the ammonia, but the wind has the power of movement and dilution of the ammonia vapor
- 6. Note the cone shaped V pattern at the point of release
 - a. Note how wind conditions affect the cloud
 - Also note how the cloud widens as the ground cools allowing the ammonia cloud to dissipate
 - c. This is important to consider when establishing a Hot Zone and Protective Action Zone





F. Weather Impacts

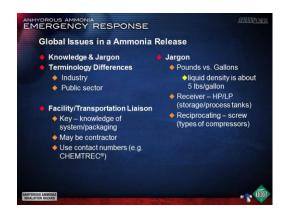
- 1. Although anhydrous ammonia's vapor density is lighter than air, it can exhibit heavier than air characteristics
 - a. High humidity such as foggy, misty, rainy conditions will keep ammonia on the ground
 - b. This picture is a live ammonia training event and Level B is being used since we are under controlled circumstances
 - c. There was a light rain falling and the vapor cloud hung low to the ground
- 2. In good weather you will see the vapor cloud reacting favorably by going up and away
 - a. You will see a hook at the top of the plume. This may hook back to the ground
 - The height of the release plume will play into how the dense gas and vapor trail will disperse

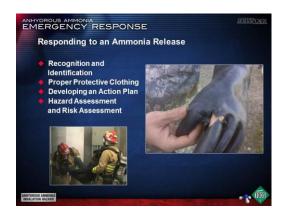


- c. Dense gas is forming 20-30 feet in the air. Those located in front of the release will not be exposed as those downwind of the release as the dense gas cloud settles to the ground before dispersing into a vapor and heading into the upper atmosphere
- d. Always be cautious about the downwind drop of the ammonia plume. It may be several hundred feet downwind in small spills or hundreds of yards downwind in larger spills

G. Environmental Impacts of Release

- 1. Use extreme caution with unmitigated solutions of aqua or anhydrous ammonia
- 2. The solution must be contained in a safe location so that the ammonia can evaporate
- 3. Aeration of the solution may allow the pH to drop to acceptable levels
- Don't allow the solution to travel into bodies of water as it is extremely dangerous to fish and wildlife
- 5. A little ammonia will drastically affect the pH of water and any run off should be contained to prevent harm





H. Global Issues in Ammonia Release

- 1. Terminology between responder and facility personnel could be an issue
- 2. Stay away from company/industry jargon.
- Some industries may refer to quantity in pounds when responders may use gallonsanhydrous ammonia's liquid density is about 5lbs per gallon
- 4. The key to good communication is to have a good liaison from the facility to communicate with

I. Response to Ammonia Releases

- Keys are recognition and identification, hazard and risk assessment, choosing proper personal protective clothing, and developing an action plan
- 2. Hazards are always higher when extreme conditions such as high pressure, high volume, and high density gas clouds are present
- The Incident Commander must assess risk and determine the proper protective equipment for the objective to be completed
- 4. Incident Action Plans and Safety Plans are both needed and usually required at a release

- 5. Understand the hazards given the situation whether an indoor or outdoor release
- 6. The glove was a Level A neoprene glove that degraded due to the cold temps. Responders were working to shut off a valve in a dense gas cloud very near the aerosol stream
- 7. Use a risk/benefit analysis before putting responders in harm's way
 - a. Can you clearly see your exit pathway?
 - b. Are you feeling any discomfort from exposure (groin, armpits, neck and head will feel the burn and sting of ammonia first)?
 - c. Calculate your risk based on what you are able to save

J. Evacuation Recommendations

- 1. Follow Emergency Response Guide Evacuation Recommendations
 - a. Small Spills: Initially isolate 100' and protect downwind 0.1 mile day/night
 - b. Large Spills: Initially isolate 500' and protect downwind 0.5 miles day and 1.4 miles night
 - c. The most risk will be within the downwind pattern



- d. Shelter in Place works well for the downwind exposure. Evacuate only if it's safe to enter the outside environment
- 2. Evacuation or Shelter in Place Considerations
 - a. To evacuate: Move laterally and upwind. Get outside the "V" since the sideline of the "V" is very defined with concentrations of ammonia
 - b. Shelter in Place: Testing has proved that there may be some value in persons who are sheltered in place turning on a shower and putting a wet wash cloth over their face to protect them from excessive amounts of ammonia
 - c. In Minot, ND 9 ammonia cars released their contents into a dense gas cloud that floated over the community.
 - d. The 911 center advised residents to move to the bathroom and turn on the shower if ammonia odor became strong in their home. Levels of approx. 200 ppm were reported





e. The Center for Toxicology and Environmental Health (CTEH) tested this method of shelter in place and found that having the shower running and using a wet wash cloth were both effective in reducing the ammonia levels to below 50 ppm

K. Placards and Warning Signs

- Domestic shipments within the US can be classified as Hazard Class
 2.2 non-flammable gas using the Green non flammable placard
- 2. Internationally ammonia is classified as a Hazard Class 2.3 poison gas, with a subsidiary warning of corrosive
- 3. The UN Number for North America shipments is UN1005
- 4. Note that there are Canadian rail cars entering the US with a special permit placard, which looks like the 2.2 hazard class but is white/black in color
- 5. NFPA 704 for storage facilities
 - a. Red diamond is for Fire Hazard
 - b. Yellow diamond is for Reactivity
 - c. White diamond is for Special Hazards





- d. Blue diamond is for Health Hazards
- e. The scale is from 0 to 4 with4 being the highest hazard
- f. The Special Hazards section could have "ALK" or "COR" for ammonia

L. Other Considerations

- 1. Avoid Trapping Liquids
 - Do not be valve turners unless you know there is pressure release protection where the ammonia may be trapped or contained
 - b. Ammonia has a high coefficient of expansion.
 - c. The photo shows a kinked line that trapped liquid ammonia and eventually blew out!
- 2. Flammability of Outdoor Releases
 - Outdoor releases do not have a high risk of flammability with ammonia
 - LEL/UEL is 16-25%. The most likely flame spread will occur while the flame is directed to a dense gas aerosol stream
 - c. The ammonia vapor will burn much like when the smoke from a hot campfire flash burns above the burning wood



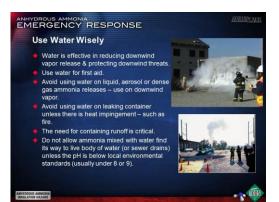


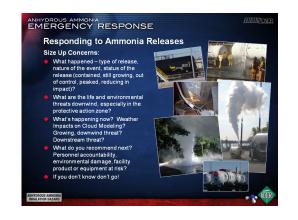
Instructor Note: The video is in the Extras file on your DVD. You must exit PowerPoint and open this video file in an external video viewer.

- 3. Flammability of Indoor Releases
 - a. With indoor releases in a confined area there is a greater chance of flammability
 - A LEL/UEL mix could form and typically indoor releases happen at industrial refrigeration processes
 - c. Contaminants such as oil can mix with the ammonia and affect the "textbook" flammability range
 - d. Indoor ammonia releases can pose potential flammability concerns
 - e. Ventilate and control ignition sources prior to entry
 - f. This picture is an example of a release that sparked a fire
- 4. Ammonia and Water
 - Ammonia loves water: One volume of water will absorb 1300 volumes of ammonia vapor
 - When ammonia moves to water located in an enclosed environment, like a tank or vessel, that movement of ammonia will cause a vacuum like the one shown in this situation. The tank integrity held up, but the tank was obviously no longer serviceable.

- c. Ammonia quickly mixes with water to form aqueous ammonia, or ammonium hydroxide, which is heavier than air and has higher pH values (up to 13.2 from 11.6)
- d. When ammonia and water mix, an exothermic reaction occurs giving off heat. The molecular heat of the reaction raises the water temperature. This can be seen by measuring the increase in temperature of water used to "blow down" or remove ammonia from a system
- e. Ammonia loves water, but if you put water on ammonia it will become "spitting mad."
- f. If ammonia is introduced into water purposefully, the reaction isn't as bad, especially if the amount of water is adequate
- g. The absorption of ammonia to water is about 1 volume of ammonia to 10 volumes of water when the solution is mixed completely at about 70°F

- Aqueous ammonia vaporization is dependent upon the temperature of the water, the amount of wind, and the amount of surface area exposed. Usually, the volume of ammonia will reduce faster as temperature, surface area, and amount of warm air are increased
- i. Discuss the vapor to water relationship: One volume of water will absorb 1300 volumes of ammonia vapor
 - i. What happens to the white cloud of aerosol and vapor in the video clip? The white cloud is a result of vaporization because of warm air and cold air mixing in the presence of humidity.
 - What happens to that air temperature difference when water mixes into the vapor cloud? It goes away.
 - iii. What happens to the ammonia? It joins with the water vapor and lays low until vaporized by surrounding air. Its pH value also increases and it can become much more irritating to the skin.





- j. The temperature of tepid water from a hose will be about 55 to 65°F. What would that do to the ammonia temperature and pressure within a vessel?
- k. When is it a good idea to put water on a vessel?
- 5. The summary message is to avoid using water on liquid, aerosol or dense gas ammonia releases.
- Water is effective in reducing downwind vapor release, but the need for containing runoff is critical. Do not allow ammonia mixed with water to find its way to a live body of water unless the pH is below local environmental standards (usually under 8 or 9)
- 7. In the bottom picture ask the class where to use water to knock down the cloud. Not on the leaking container, but downwind to protect "downwind threats" to the right of the picture.
- 8. The next concern would be to dike or contain the run off.
- 9. Size Up Concerns:
 - a. What happened type of release, nature of the event, status of the release (contained, still growing, out of control, peaked, reducing in impact)?



- b. What are the life and environmental threats downwind, especially in the protective action zone?
- c. What's happening now? Growing, downwind threat? Downstream threat?
- d. What do you recommend next? Personnel accountability, environmental damage, facility product or equipment at risk?
- e. If you don't know, don't go!

M. Control and Contain- Tarp and Cover

- 1. This is a tarp and cover control/containment method for some ammonia release incidents
 - The release point is covered with a tarp (basic tarp you can buy at a local hardware supply – polyethylene or polypropylene)
 - b. The tarp covers the release point and the escaping dense gas cloud will condense to liquid phase product which will then cool the container and release point
 - c. We learned that there is a direct pressure/temperature relationship with ammonia and if the temperature drops, the pressure drops



- d. Your downwind concerns are also minimized in that the release is controlled/ contained to the local release area
- 2. This is not a cure all tactic. The ammonia is controlled or contained at this point
- 3. You may then start to get liquid ammonia pooling under and near the tarp. Do not walk through liquid pools
- 4. What is occurring under the tarp while the dense gas flows around the vessel?
 - a. The cold gas will lower the pressure in the vessel and the condensation of the aerosol stream will result in liquid ammonia saturating the ground rather than to go downwind to threaten life hazard...if there is no life or environmental hazard on the downwind then allowing the ammonia to escape to atmosphere might be the best solution
 - Notice how the dense gas cloud stays low as the gas begins to vaporize to atmosphere on the downwind side





- c. On a dry day the dense gas cloud is not as evident although the vapor risk may still be very high on the downwind side
- 5. You can see in the picture that the tarp has minimized the exposure area.
 - The leak point or leaking container will be cooled from the ammonia – if we drop temperature the pressure in the container will also drop.
 - b. Fully contained with the first tarp; secondary tarps may be helpful...now we can find the source of the release and control the flow... shut it down!
 - c. A positive pressure ventilation fan is helpful in directing the dense gas away from the responders as they place the tarp and work on controlling the release... it's also a good first step to getting fresh air to a victim that may be collapsed in the downwind area
- 6. Placing the tarp from a distance, outside the dense gas cloud, can be accomplished with Level A or even Level B PPE (if the responders stay out of the dense gas and aerosol part of the release)



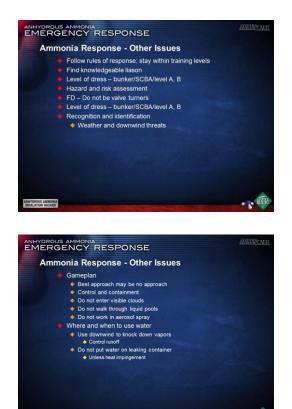
- 7. A fan used to support the responders is very valuable
- 8. Responders must be trained in this procedure before attempting it

N. Large Containers and Rail Tank Cars

- 1. Anhydrous ammonia tank cars have a capacity of over 33,000 gallons; however with the required outage, they typically contain less than 30,000 gallons – 160,000 pounds
- Capping kits may or may not work on tank cars – depends if there is enough spacing around the valve flange
 - a. The middle picture shows enough spacing
 - b. The bottom picture may not have enough space around the valve flange to cap a leaking valve
- 3. Tank cars will always have:
 - a. 2 liquid valves which point towards the ends of the car
 - A single vapor valve will be perpendicular to the liquid valves and point toward the side of the car
 - c. A pressure relief valve
- 4. Could have other valves such as a gauging device, thermometer well and sample tube line



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 Cargo trailers (tractor trailer versions) could range in size from 3.500 gallons to almost 12,000 gallons

6. Nurse tanks range in size from 500 gallons to over 1,000 gallons

- O. Ammonia Response Other Issues
 - 1. Review the points on the slide
 - Don't be valve turners since we do not want to trap liquid ammonia without being able to relieve pressure
 - 3. Ensure proper personal protective pquipment is used
 - 4. Review where and when to use water and always contain run off
 - 5. Evaluate tarp and cover as a control and containment method for incidents

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EMERGENCY RESPONSE CONTACT NUMBERS

Burlington Northern S	anta Fe 800-832-5452
Canadian National	800-465-9239
Canadian Pacific	800-716-9132
CSX Transportation	800-232-0144
Kansas City Southern	877-527-9464
Norfolk Southern	800-453-2530
Union Pacific	888-877-7267
CHEMTREC®	800-424-9300
CANUTEC	613-996-6666 (call collect)

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The materials developed for the Anhydrous Ammonia Training Tour 2011 are intended to provide general understanding and guidance to emergency responders in addressing anhydrous ammonia incidents. They include information about the chemical and helpful considerations that the emergency responder can employ when faced with such an incident. The materials are in no way intended to be prescriptive or otherwise recommend specific procedures on how to respond. Emergency responders are encouraged to consult with the product manufacturer, carrier and other experts when assessing and managing any incident involving anhydrous ammonia.