ANHYDROUS AMMONIA SPILLS

Last month AristaTek published an article on chlorine spills. AristaTek posed the question, are the models predicting release of a toxic gas and resulting dispersion any good? AristaTek examined a popular pool evaporation model used in ALOHA and in the PEAC tool and compared the chlorine evaporation rate as measured by experimental test with model predictions. Comparisons were also made in chlorine gas dispersion predictions as a function of distance downwind between popular models in the public domain, the 2004 Emergency Response Guidebook (ERG), and PEAC tool predictions. A conclusion was that the PEAC tool results were similar to answers predicted the models examined, but there were differences between the models during stable, clear nighttime conditions.

Let us do the same type of analysis of anhydrous ammonia spills. We will compare experimental liquid ammonia evaporation test results with model predictions and compare PEAC tool gas dispersion results with models in the public domain and with the 2004 ERG published protective action and initial isolation distances.

Background Information: Anhydrous Ammonia Production and Storage

Roughly 100 million tons of anhydrous ammonia are produced worldwide annually. Almost all is used to produce nitrogen-based fertilizers or used directly by farmers. Other uses include synthesis of industrial chemicals such as polymers, manufacture of explosives, and ammonia-based cleaners. Nitrogen-based fertilizers made from anhydrous ammonia include urea, ammonium nitrate, urea-ammonium nitrate solutions, ammonium sulfate, and ammonium phosphate. Anhydrous ammonia is manufactured from natural gas (the nitrogen part of ammonia comes from the nitrogen in the air); about 80 or 90% of the anhydrous ammonia cost is reflected in the price of natural gas. Peak anhydrous ammonia production in the United States occurred in 1998 (16.8 million tons sold, excluding quantities used to make nitrogen-based fertilizers at production facilities, total including nitrogen based fertilizers roughly 23 -24 million tons). Since 1998, the United States has been importing greater amounts of anhydrous ammonia (including nitrogen-based fertilizers) and producing less domestically because the price of natural gas is cheaper in producing countries. About 45% of nitrogen-based fertilizers and ammonia comes from Canada. Major worldwide production facilities are in Russia, the mid-East, China, and Venezuela.

Anhydrous means “without water”. Anhydrous ammonia is a gas at ambient temperature and pressure; its chemical formula is NH_3. This gas is very soluble in water. The solubility of ammonia in water is about 54 grams per 100 milliliters. A solution of ammonia in water is called “ammonia water” or ammonium hydroxide, and is usually written as the chemical formula NH_4OH. Some household cleaners contain 5 to 10% ammonia by weight.

Anhydrous ammonia gas can be compressed and liquefied. At a temperature of 70^{o}F (21^{o}C), anhydrous ammonia will liquefy at 128.8 pounds per square inch absolute (psia), or about 114 pounds per square inch gage (psig), more or less depending upon the elevation. Storage of liquid ammonia under pressure is much more feasible than storing the gas. At 70^{o}F, one pound of liquid ammonia occupies a volume of 0.0263 cubic feet compared with 2.31 cubic feet for the gas not under pressure. One cubic foot of ammonia liquid can produce about 855 cubic feet of ammonia gas.

Liquid anhydrous ammonia is stored or transported in tanks under pressure. The tanks must be fabricated and designed to meet ANSI guidelines provided in their document, “Safety Requirements for Storage and Handling of Ammonia”. The tanks are not completely filled with liquid ammonia, but might contain a headspace of at least 15% (by volume) of ammonia and inert gases. Anhydrous ammonia tanks used as fertilizer on farms may have a 3000-gallon capacity and rated at 250-psig pressure. Anhydrous ammonia tanks transported by truck and railcar have larger capacities. The sketch below shows an anhydrous ammonia nurse tank, which might be used at a farm facility.

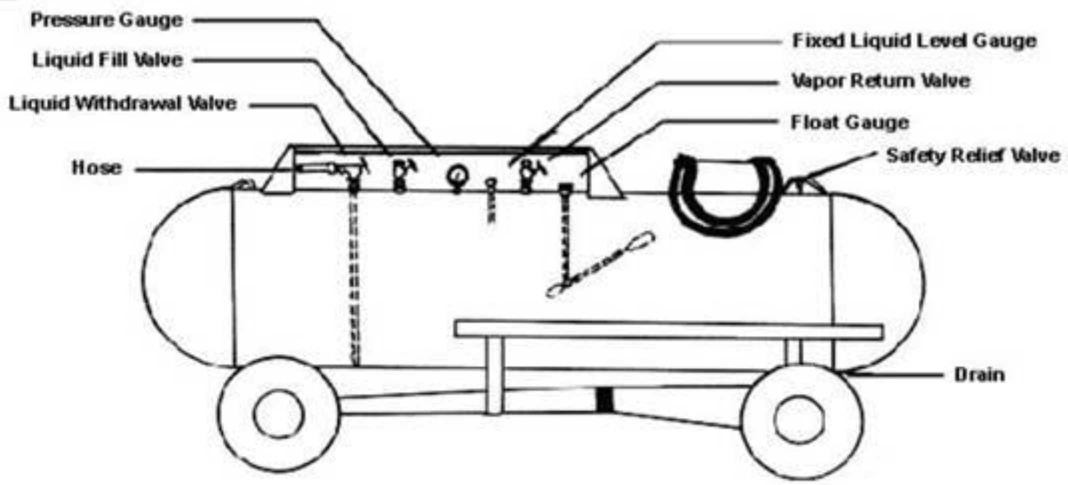


Figure 1: Anhydrous Ammonia Nurse Tank (from Univ. of Nebraska Coop. Extension Document EC94-738)

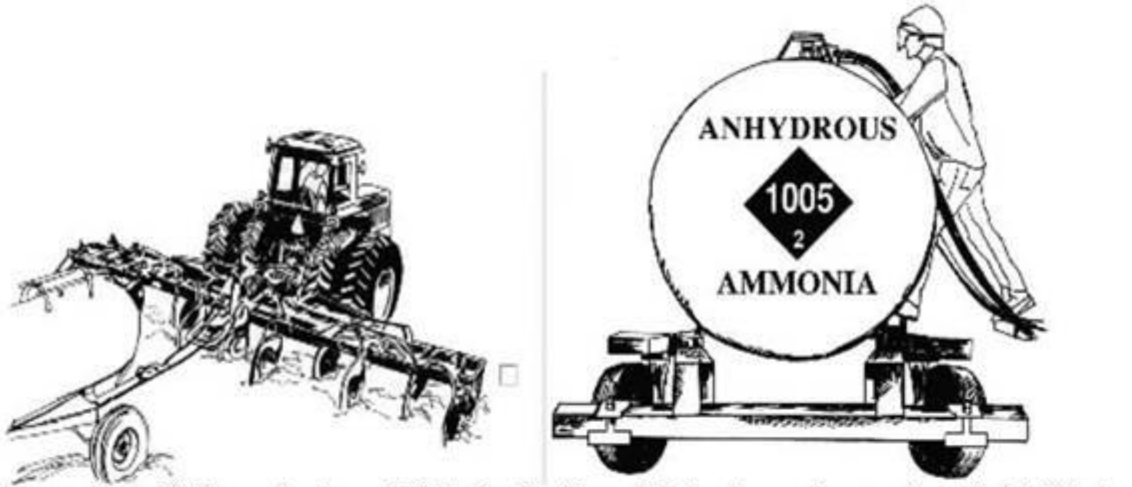


Figure 2. Left: Nurse tank and Field Application of Anhydrous Ammonia. Right: Worker in Protective Clothing Attaching Transfer Lines (from same document as figure 1)

Figure 3. Left: Rail Car containing Anhydrous Ammonia. Right: Tanker Truck
(photo from http://home.comcast.net/~pchristou/2004June.html)

What Happens if Liquid Ammonia is Spilled?

Let’s say that there is a breach in an ammonia transfer line or a storage or transport tank is compromised and liquid ammonia spills. The pressure is release and the liquid ammonia evaporates. As the ammonia evaporates, heat is extracted from the surroundings. The ammonia temperature drops. Liquid ammonia boils at about -32°F (give or take a few degrees depending on the elevation above sea level). If the spill is large enough, this temperature will be quickly reached, and the remaining ammonia liquid will be chilled even further as more heat is extracted during the evaporation process.

The gaseous ammonia released from the tank and subsequent evaporation from the liquid pool results in a cloud of gaseous ammonia which travels downwind. We will divide this problem up into two parts:

- Do models in the public domain accurately predict the evaporation rate?
- How does the gaseous dispersion model in the PEAC tool compare with other models in the public domain?

Measurement of Liquid Ammonia Pool Evaporation Rates

The owners of AristaTek while employed by the University of Wyoming Research Corporation (UWRC), d/b/a/ Western Research Institute, made arrangements with the HazMat Spill Center (HSC) located at the Nevada Test Site to spill liquid ammonia in a one square meter pan. Two pans were used. This work was part of a larger contract funded by the U.S. Department of Energy in 1995. The pans were located inside a wind tunnel at the site; the wind tunnel allowed a controlled environment by which measurements and video could be taken without the extraneous complications of sunlight, wind shifts, and precipitation. A large fan at the end of the wind tunnel allowed a controlled wind flow across the pan. There were also turbulence promoters upwind of the pans set in a predetermined pattern as recommended by several consultants familiar with wind flow and atmospheric dispersion studies.

Figure 4. Exterior of Wind Tunnel at the HSC Used for Ammonia Liquid Evaporation Tests

We (the people who later founded AristaTek) had available the HSC for a very short time because of tight scheduling with other clients who also wanted to use the facility; consequently there was time to do only two tests spilling liquid ammonia (on April 5-6, 1995). Unfavorable meteorology prevented another test on April 7-8. Another test had been done on April 4 spilling liquid chlorine. The major objective of the tests was to see if the pool evaporation rate for spilled cryogenic hazardous chemicals agreed with the pool model evaporation predictions used by ALOHA. The ALOHA model is used in EPA's CAMEO software.

The ammonia was delivered to the evaporation pan from a one-ton capacity tank; a vent chamber in line ahead of the pans allowed removal of ammonia gas so only liquid ammonia was delivered to the pan. The system was heavily instrumented (weighing sensors, wind speed, temperature, video, etc.), and could be viewed and controlled from the safety of a control room about 1 mile from the test. There were heaters under the pan which allowed variation of the pool temperature. Approximately 12 kg of ammonia evaporated as gas for every 33 kg of liquid ammonia delivered to the pans, plus another 5 kg ammonia evaporated during the initial chilling of the pans before the liquid pooled. As evaporation from the pools continued, the pool temperature dropped well below the liquid ammonia boiling point temperature. Bulk pool temperatures as low as -69^{o}C (-92^{o}F) were measured. Air temperature varied between 17 and 20^{o}C. Ammonia pool skin temperatures, as measured by an optical pyrometer, were several degrees colder than the pool bulk temperature, with readings as low as -75.5^{o}C (-104^{o}F) obtained. The video of the tests showed a white, slushy solid which appeared to form at the top of the evaporating pool and sank to the bottom. The amount of "ice" was not enough to greatly interfere with the evaporation rate measurements. We do not know whether the "ice" was the result of water vapor absorbed by the chilled ammonia or whether the ammonia pool was starting to freeze. The freezing point of anhydrous ammonia is -75^{o}C (-103^{o}F). Evaporation rate measurements were collected for various pool temperatures between -55^{o}C and -68^{o}C (-67 to -90^{o}F). Some typical readings (averaged) were 0.249 kg/min/m^2 at -58^{o}C , 0.131 kg/min/m^2 at -65^{o}C, and 0.114 kg/min/m^2 -67^{o}C. The results compared very favorably with the evaporation model used in ALOHA. If bulk pool temperature is used as a basis, the measured evaporation rate was either the same or slightly lower than ALOHA model predictions. If skin temperature is used as a basis, the measured evaporation rate was slightly higher than ALOHA model predictions.

The National Oceanic and Atmospheric Administration (NOAA) out of Seattle, WA, sent a representative, Roy Overstreet, to observe the tests. NOAA was responsible for writing the developmental document upon which ALOHA was based. The reference citation is,

Reynolds, R.M. 1992. ALOHA™ Theoretical Description. Report NOS ORCA-65. National Oceanic and Atmospheric Administration, Seattle, WA.

Roy Overstreet concluded that the evaporation test results matched ALOHA predictions. He was able to gather the measurements in the control room while the experiments were underway. We also concluded the same thing after processing the data gathered from the tests.

Because of the test agreement with ALOHA predictions, the founders of AristaTek made a decision when the PEAC tool was developed to use the same evaporation algorithms for pool evaporation that ALOHA used. The pool evaporation algorithms are available in the public domain in peer-reviewed literature.

One major unknown when using an evaporation model is the matter of heat balance. If there is significant heat input, as what would happen if the ammonia or other liquid is spilled on a hot surface, the evaporation rate will be higher than predictions, at least initially. As the ground becomes chilled, the evaporation rate will become closer to predictions unless there is an extraneous circumstance as in a fire. By convention, both the ALOHA model and the PEAC tool assume that the surfaces quickly become chilled and heat input is low.

Model Comparisons for Ammonia Cloud Gas Dispersion.

Massive ammonia releases have occurred in the past. For example, on January 18, 2002, at Minot, North Dakota., 15 anhydrous ammonia rail cars derailed during the night (1:34 AM) releasing about 230,000 gallons of anhydrous ammonia from eight tanks. The resulting ammonia vapor cloud was described as 5 miles long, 2.5 miles wide, and 350 feet high. There was one death, 330 people were treated initially, and 1605 people were treated for recurring ailments. Winds were from the SW at 6 or 7 mph. At this time of night and because of the cold temperatures, shelter-in-place was the only option for the general public. Because of the chilly temperatures (10°F), the initial gas release and the pool evaporation rate was undoubtedly less than if the accident occurred during the summer. But basic information such as the liquid pool area required to model a release was not available. There were also problems in communicating response information to the general public. This event was the subject of an earlier PEAC Newsletter article which was printed in May 2003.

For the purpose of comparing gas dispersion models, we will assume a hypothetical ammonia rail car accident where the tank car is ruptured and all of the ammonia is spilled. The rail car contains 40 U.S. tons (14060 gallons; 36287 kg) of anhydrous ammonia. All of this is spilled onto the ground.

A common mistake is to assume an instantaneous release where all of the ammonia is released to the air at once. The gas dispersion model is run in the instantaneous mode. The model then seriously over predicts air concentrations as a function of distance. Critics conclude that the model is no good because of the overprediction.

But that is not what happens. When the tank is ruptured, there will be an initial gas release because of the release in pressure. As the liquid escapes from the tank and starts to pool on the ground, more gaseous ammonia is formed. The ground will chill fairly quickly as the liquid ammonia evaporates. For the purpose of modeling, this is a two-part problem. The first part is an instantaneous gas release. The second part is evaporation at a "constant rate" from a liquid pool. There will be a transition between the initial instantaneous gas release and the "steady state" evaporation from the liquid pool, and finally, the gaseous ammonia emissions will trail off at the last liquid ammonia evaporates.

This makes modeling difficult. The modeler must know (1) the amount of gaseous ammonia which initially forms when the pressure is released and the liquid ammonia initially contacts the ground, (2) the liquid pool area, and (3) meteorology (wind speed, temperature, and cloud cover). This information is rarely available. Usually what happens is that the modeler either assumes all the ammonia is released instantaneously (which grossly over predicts ammonia concentrations in the air and evacuation distances) or all of the liquid ammonia covers the ground to a depth of 1 cm, and calculate a pool area knowing the amount spilled.

Another option is to use the initial isolation and protective action distances published in the 2004 Emergency Response Guidebook (ERG). The 2004 ERG lists Initial Isolation Zone and Protective Action Distances for hazardous chemicals involved in transportation accidents. This guidebook is published jointly by Transport Canada, U.S. Dept. of Transportation, and Secretariat of Transport (Mexico), and is available at http://hazmat.dot.gov/pubs/erg/erg2004.pdf.

The user need only consider four categories for each chemical when looking up the Initial Isolation Zone and Protective Action Distances in the Emergency Response Guidebook. The categories are (1) small spills, daytime conditions, (2) large spills, daytime conditions, (3) small spills, nighttime conditions, and (4) large spills, nighttime conditions. A breach in an anhydrous ammonia railcar is a large spill. The display for anhydrous ammonia is shown in Figure 5.

Figure 5. Initial Isolation and PAD for Anhydrous Ammonia

English units:

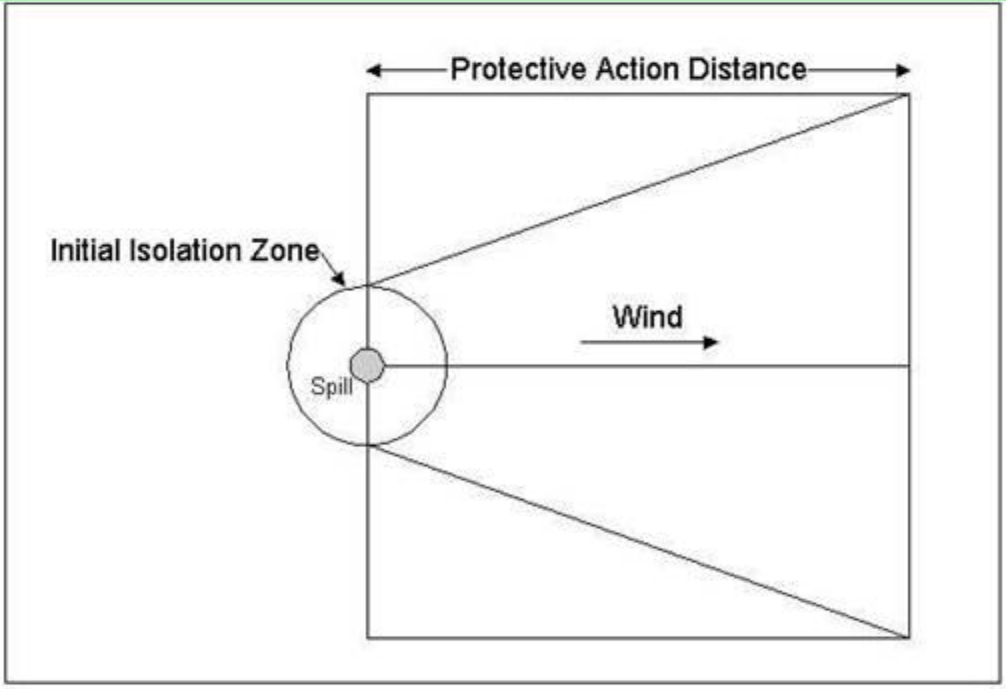
Initial Isolation and

Small Spills			Large Spills		
Initial Isolation	Day	Night	Initial Isolation	Day	Night
100 ft	0.1 mi	0.1 mi	200 ft	0.4 mi	1.4 mi

Metric units:

Initial Isolation and

Small Spills			Large Spills		
Initial Isolation	Day	Night	Initial Isolation	Day	Night
30 m	0.1 km	0.1 km	60 m	0.6 km	2.2 km



What is a large spill and what is a small spill? For most hazardous chemicals, the Emergency Response Guidebook considers anything greater than 55 or 60 gallon as a large spill. A 40-ton rail car is a large spill, but a breach in a one-ton ammonia tank would also be considered a large spill. The information displayed in the Emergency Response Guidebook for ammonia looks like the chart in figure 5 The information can be displayed in English or metric units.

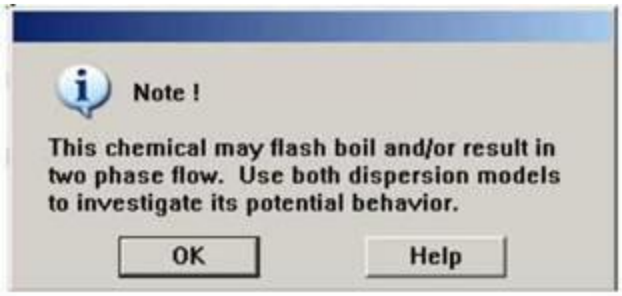
Let us get back to model comparison. We need to estimate the amount of vapor formed when the rail car tank pressure is released and how much liquid pools on the ground. The tank is assumed to be at 70°F initially and then ruptures. The fraction of ammonia vapor formed can be calculated from an enthalpy (heat) balance, e.g., if x = mass fraction of ammonia gas formed per lb of original liquid in the tank, 120.5 btu/lb is the enthalpy of liquid ammonia at 70°F, 600 btu/lb is the enthalpy of the vapor at ammonia's normal boiling point, and 8 Btu/lb is the enthalpy of the liquid at ammonia's normal boiling point, then

$120.5 = 600x + (1-x)\,8$

x = 0.19
Yes, the liquid spilled will cool further than the boiling point, and there will be heat extracted from the surroundings resulting in more ammonia vapor.

Cranking through the numbers, 0.19 times 40 U.S. tons of ammonia equates to 7.6 tons, or 6895 kg. We will allow for a 15% hangup in the tank which also leaves the tank and vaporizes at a slower rate, or 5850 kg which vaporizes quickly. We will call it a 6000 kg instantaneous release in round numbers.

The PEAC tool allows the user to estimate a release rate based on a hole size in a tank or a sheared-off pipe. For the purpose of model comparison, we will assume all of the tank contents is released at once as in the case of a catastrophic rail accident or a terrorist bomb. But only 6000 kg of the ammonia vaporizes quickly. The rest pools on the ground and evaporates at a slower rate.

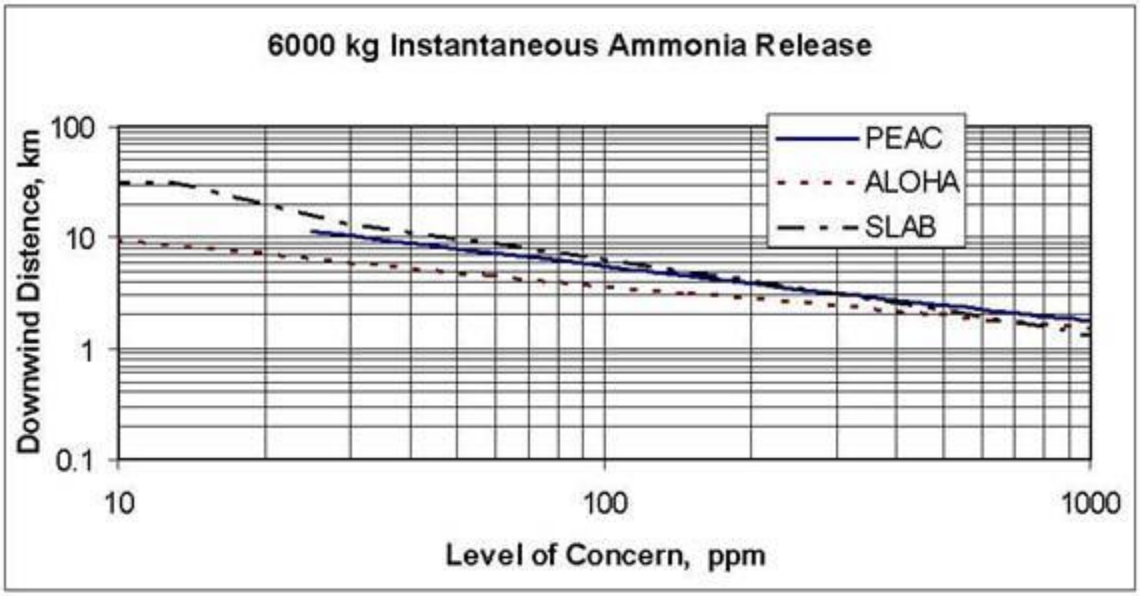

Note !

This chemical may flash boil and/or result in two phase flow. Use both dispersion models to investigate its potential behavior.

The ALOHA tool displays a warning message as shown on the left that the chemical may flash or boil, and that the user might consider both [dense gas and passive] dispersion models, but there are no instructions as what to do.

We will compare PEAC tool predictions with two other popular model predictions for a 6000 kg instantaneous release of ammonia vapor. We will use metric rather than English units. The wind speed for all of these comparisons is 5 meters/second (measured at a 2-meter height), rural/cropland/farmland-type terrain, overcast skies, 70°F ambient temperature, daytime. All of these models calculate a downwind distance for a user-specified Level of Concern. The Level of Concern is the concentration of ammonia at the center of the ammonia vapor cloud. As the ammonia vapor cloud travels downwind, it becomes dispersed and more dilute. Figure 6 displays a logarithmic plot of distances in kilometers as a function of Levels of Concern for the PEAC tool and two popular models in the public domain.

Figure 6: Downwind Distance from Instantaneous 6000 kg Ammonia Release for Various Ammonia Levels of Concern.



The ALOHA model is available at no cost from the U.S. Environmental Protection Agency. Version 5.3.1 of the ALOHA model can be downloaded at http://www.epa.gov/ceppo/cameo/aloha.htm. The PEAC tool is available from AristaTek, at http://www.aristatek.com/. SLAB is a dense gas model developed by Lawrence Livermore National Laboratories under U.S. Dept. of Energy contract. SLAB is available from a number of sources such as http://www.weblakes.com/lakeepa4.html.

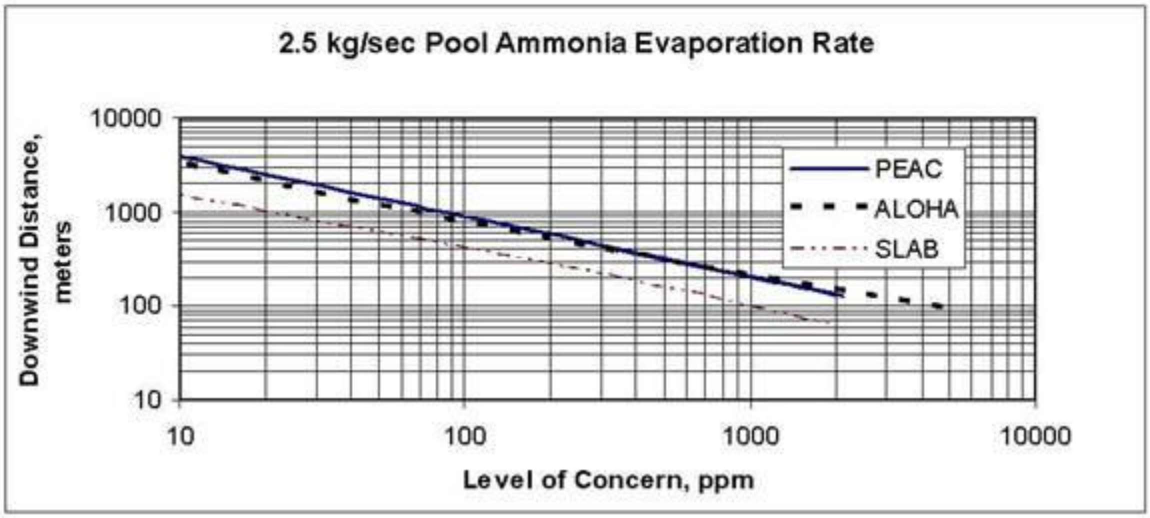
The anhydrous ammonia which does not instantaneously vaporize is assumed to collect on the ground and form a liquid pool. The model user must specify a pool area. If the pool area is not known, usually a 1 cm depth is assumed, which calculates (in round numbers) to about 4000 square meters. In the real world the liquid ammonia will follow the terrain collecting unevenly in pockets or ditches along the railcar right-of-way; a 1 cm even depth is not realistic. An estimate of the pool area is very difficult for a responder to obtain. Industry storing large stationary tanks containing hazardous liquids is required to have dikes to contain the liquid in the event of a spill, but transportation accidents are a different situation. For the purpose of model comparisons, we will assume that the pool area is 1000 square meters (equivalent to a collection in a ditch 50 feet wide and a little over 200 feet long along the railroad right-of-way).

Both the PEAC tool and ALOHA contains algorithms that calculate a pool evaporation rate based on a heat inventory balance. The user does not need to specify a pool temperature. As we have seen from the experimental test (see figure 4), the pool temperature can drop way below the normal boiling point of ammonia. However other models such as SLAB do not have this pool evaporation rate calculation capability. We will bypass this part of the calculation in the PEAC tool and ALOHA and specify a release rate of 2.5 kg/sec. from the 1000 m^2 pool. [e.g. 0.15 kg/min/m^2 times 1000 m^2 divided by 60 seconds/minute = 2.5 kg/sec].

We will compare PEAC tool predictions with two other popular model predictions for a 2.5

kg/s ammonia release from an evaporating pool.. The same meteorology and conditions as the "instantaneous" release graphed in figure 6 applies. All of these models calculate a downwind distance for a user-specified Level of Concern. The Level of Concern is the concentration of ammonia at the center of the ammonia vapor cloud. As the ammonia vapor cloud travels downwind, it becomes dispersed and more dilute. Figure 7 displays a logarithmic plot of distances in meters as a function of Levels of Concern for the PEAC tool and two popular models in the public domain.

Figure 7: Downwind Distance from Evaporating Pool for Various Ammonia Levels of Concern, Evaporation Rate 2.5 kg/s



For the evaporating pool situation with ammonia, both the PEAC tool and the ALOHA model give essentially the same answers. The SLAB model predicts a smaller downwind distance match to a level of concern. The reason that ALOHA and the PEAC tool give essentially the same answers for this situation is that ammonia gas dispersion is treated passively (as opposed to treating as a dense gas) and the same algorithms for passive gas dispersion are used in the PEAC tool and ALOHA (there are some differences between PEAC tool and ALOHA for the stable nighttime condition). The SLAB model uses different algorithms, and different results will be obtained depending on the geometry of the evaporating pool.

What Should Be the Level of Concern?

The Emergency Response Planning Guidelines (ERPG) are most frequently used as the Level of Concern. ERPG numbers are developed by the Emergency Response Planning Committee of the American Industrial Hygiene Association (AIHA). They are defined as follows:

ERPG-1: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor. For ammonia, this is 25 ppm.

ERPG-2: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. For ammonia this is 150 ppm.

ERPG-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. For ammonia this is 750 ppm.

The odor threshold for ammonia varies with individuals but is about 17 ppm.

The 2004 ERG (see figure 5) uses the ERPG-2 as the Level of Concern for calculating a Protective Action Distance. For ammonia, this is 150 ppm. Let us compare the PADs based on 150 ppm ammonia as the Level of Concern for all of the methodologies that we have examined.

Table 1: Protective Action Distances for to 150 ppm Level of Concern

Methodology	**PAD, km**
2004 ERG, large spills, daytime	0.6
6000 kg Instantaneous Release, PEAC tool	4.5
6000 kg Instantaneous Release, SLAB	4.6
6000 kg Instantaneous Release, ALOHA	3.0
2.5 kg/s Pool Evaporation, PEAC tool	0.65
2.5 kg/s Pool Evaporation, ALOHA	0.65
2.5 kg/s Pool Evaporation, SLAB	0.34

The 2004 ERG is not a sensitive tool; it gives a guideline for typical transportation accidents. It does not give PAD estimates for a catastrophic sudden release of a rail car containing 40 tons of liquid anhydrous ammonia. Even with a catastrophic release of ammonia from a rail car, only about 20% would be released as a vapor and the rest would pool on the ground and evaporate more slowly. The PADs from the pool evaporation rate were about the same as the 2004 ERG PAD for large spills, but this is a coincidence for the example given.

The concentrations graphed are maximum, centerline concentrations. If a person moves crosswind from the chemical cloud centerline, the concentrations will usually rapidly drop off.

What can we conclude from all this?

- In real accidents responders rarely have all the necessary information required to run a gas dispersion model. Reasonable guesses must be made. One of the biggest unknowns is the release rate to the atmosphere. Usually first responders can’t even get close to the site to determine exactly what is happening.
- Reasonable guesses must be made as to the release rate and meteorology. If the responders guess too conservatively (e.g. all of the chemical released at once or within a short period of time), critics may say that the model is too conservative.
- The pool evaporation model used by ALOHA and which is also in the PEAC tool accurately predict the evaporation rate of liquid ammonia.