A Review of Models for Predicting the Dispersion of Ammonia in the Atmosphere

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The state-of-the-art of the modeling of accidental releases of anhydrous ammonia to the atmosphere.

INTRODUCTION

This paper reviews the state-of-the-art of the modeling of accidental releases of anhydrous ammonia to the atmosphere. This topic was extensively reviewed some years ago [1, 2]. Since then, new experimental work has become available and further modeling work has been done; another review of the subject is timely. The discussion that follows is tied closely to the mode of release—the way in which ammonia is released to the atmosphere. It is well established that the mode of release can significantly affect the density and subsequent atmospheric dispersion. Several modes are examined, as illustrated on Figure 1.

For each, there is a careful discussion of the source term for the atmospheric dispersion model and an assessment of whether good modeling capability exists. Note that it is not my purpose to review, or even mention, all available atmospheric dispersion models—that would be too lengthy an undertaking. Readers interested in further modeling details should begin by consulting the Center for Chemical Process Safety’s “Guidelines for Use of Vapor Cloud Dispersion Models” [3] and the proceedings of the 1987 International Conference on Vapor Cloud Modeling [4].

At first sight, it is to be expected that ammonia will disperse as a buoyant plume. Its molecular weight is ~17,

100
Figure 1. Some conceivable release mechanisms [12].
compared with \( \approx -29 \) for air. Even at its atmospheric boiling point of \( \approx -33°C \), its vapor density is \( \approx 0.9 \) kg m\(^{-3}\) compared with \( \approx 1.2 \) kg m\(^{-3}\) for air at 20°C. However, there is abundant evidence from experiments [5, 6] and from accidental releases [7–10] that ammonia and air can sometimes form mixtures that are denser than the surrounding atmosphere.

Haddock and Williams [11] have shown that if ambient air, wet or dry, is mixed with pure ammonia vapor, the mixture is always less dense than the surrounding air. If a fraction \( F \) of the total amount of airborne ammonia is initially in the form of liquid droplets, then there is a critical value of \( F \), in the range 4–8%, up to which a dry air/ammonia mixture will always be buoyant. If this critical value of \( F \) is exceeded, however, the resulting mixture is always denser than air, partly because the droplets themselves contribute to the density and partly because, as the droplets evaporate, the mixed air is cooled. For moist air, the corresponding critical value of \( F \) is 16–20%. Interactions between water and ammonia are exothermic, so that a mixture of ammonia and moist air is warmer and less dense than a mixture of ammonia and dry air, all other factors being equal.

The fact that ammonia can be part of vapor clouds that vary from buoyant through denser-than-air is thus easily explained by reference to whether the mode of release leads to a substantial fraction \( F \) of ammonia droplets. For convenience, Figure 1 has been reproduced from reference [12]; it gives a simplified pictorial representation of the possible modes.

**MODES OF RELEASE**

**Pressurized Tank—Small Hole in Vapor Space**

In this context, the definition of a small hole is that \( R = a_s/A_s < 1 \), where \( a_s \) is the area of the hole and \( A_s \) is the area of the liquid surface (see Figure 1A). For anhydrous ammonia, stored in a tank at ambient temperature, pure buoyant vapor is likely to emerge at sonic velocities. There are well established formulas for the rate of release of gas jets [3]. Models for the dispersion of buoyant jet releases are also well established [13].

**Pressurized Tank—Large Hole in Vapor Space/Catastrophic Failure**

If a large hole should suddenly appear in a tank containing liquefied ammonia under pressure, the pressure above the surface is relieved instantaneously (see Figure 1B). As a result, bulk boiling occurs and most, if not all, of the contents of the vessel can be flung into the air. For ammonia initially at 20°C, simple thermodynamic considerations show that the heat carried by the liquefied gas is sufficient to vaporize about 20% of the contents of the vessel. The remaining 80% stays as a liquid and much of this liquid may become airborne as a cloud of finely fragmented liquid droplets. This general picture is confirmed by experiments on ammonia [5, 6, 14]. Thus, in this case, the droplet fraction \( F \) referred to above is about 80%, well above any critical value for heavy vapor effects.

During the bulk boiling and expansion, considerable turbulence is generated and much air is entrained almost at once, of the order of ten kg of air for every kg of ammonia. This mixing ratio of ten agrees well with observations based on reports of accidents [15]. This amount of air is sufficient to vaporize the liquid droplets of ammonia. The resultant mixture is cold, typically at or near the atmospheric boiling point of ammonia, and is denser than the surrounding atmosphere. Subsequently, it behaves as a dense, slumping puff. In recent years, heavy vapor puffs have received considerable experimental attention, the most relevant case for large scale releases being the Thor- nery Island Experiments [16]. It has been demonstrated that simple "box" models fit the Thorney data quite well. There are several box models in the literature, see Hanna and Drivas [3] for further discussion. Thus, the present case—that of catastrophic failure of a pressurized ammonia storage vessel—is apparently one that can be modeled with relative confidence.

**Pressurized Tank—Intermediate Hole in Vapor Space**

There is a range of intermediate hole sizes over which the resulting ammonia-air mixture changes from being buoyant to being denser-than-air (see Figure 1C). Experimental work on the depressurization of steam liquefied under pressure has shown that a hole with \( R \approx 0.01 \) qualifies as large since the bulk of the contents of the experimental vessel escaped when an orifice of that size was opened [1].

Considerable relevant work on the characterization of the release has been done by the AICHE's DIERS (Design Institute for Emergency Relief Systems) program [17]. Any of up to four flow regimes through the orifice is possible.

1. Pure vapor—already discussed for a small hole
2. Bubbly flow regime in which the liquid phase is continuous with discrete bubbles.
3. Churn turbulent flow regime in which the liquid phase is continuous with coalesced vapor regions of increasing size.
4. Droplet flow regime in which the vapor phase is continuous with discrete liquid droplets.

The transition between these various flow regimes occurs with increasing volumetric vapor flux, which in the present context depends on \( R = a_s/A_s \). The transition is also influenced by fluid characteristics and by the presence of impurities. In the DIERS program, the above phenomena were studied in order to derive methods for sizing emergency relief valves. The DIERS literature is too voluminous to discuss here. Work still remains to be done to establish how the results of the program can be made directly applicable to atmospheric dispersion. This case of the intermediate hole size remains one of the least understood of those illustrated on Figure 1.

**Releases from the Liquid Space of a Pressurized Container**

Figure 1D shows several possible ways in which ammonia might be released from the liquid space of a pressurized container. Jet 1 illustrates the case of a wall tank rupture, which was simulated by the experiments at Frenchman Flat [6] in which ammonia stored in two 36m road tankers was fed via a 6-inch internal diameter pipe through an orifice plate chosen so that the ammonia remained liquid upstream. The ammonia flashed rapidly on emerging into the atmosphere and became 1–2m in diameter almost at once. In three of four experiments, no ammonia rained out onto the ground, so that the airborne droplet fraction \( F \) was about 80%. In a fourth trial, a liquid pool was formed that contained only a small fraction, about 10%, of the ammonia discharged. In each trial, the ammonia formed a heavy mixture with air, with gravity spreading being apparent within 20m of the source. Thus, the Jet 1 ammonia vapor cloud has many of the characteristics of the puff formed in the case of catastrophic failure of a vessel, with the exception that it is initially a jet with well-defined direction.

Jets 2 and 3 on Figure 1D illustrate the escape of liquid through a pipe. There are three main types of flow to such an outlet. The first is liquid flow, as discussed above for a
tank wall rupture or a short pipe. Second, the flow at the outlet may be two-phase, with the liquid and vapor in thermal equilibrium. If the flow is choked at the outlet, it will be superheated. Equilibrium flow results in smaller discharge rates than does liquid flow. Third, there is a continuum of cases for which the flow at the outlet is two phase but the liquid and vapor phases are not in thermal equilibrium. These cases have intermediate flow rates.

Experimental work addressing Jets 2 and 3 \cite{5, 18} shows that the resulting vapor clouds are always denser-than-air and that no rain-out of droplets occurs. Jet 4 illustrates the case of impingement onto a surface, in which case up to about 70–80% of the liquid droplets may collect in a pool on the ground. Nonetheless, the remaining plume still contains enough airborne droplets to be denser-than-air \cite{5}. There are no theoretical models for the prediction of the recovery fraction.

Escapes from the liquid space of a pressurized container require the study of a number of complex phenomena, including:

1. The rate of release of ammonia in the various configurations illustrated on Figure 1D.
2. The flashing of superheated liquid and the formation of ammonia droplets.
3. The entrainment of air into denser-than-air, high velocity, two-phase momentum jets.
4. The evolution of the jet into a "conventional" heavy vapor plume.

The question of the rate of release has been addressed by several authors and was summarized by Wheatley \cite{19, 20}, who expresses some skepticism about whether the literature currently covers the full spectrum of possible release rates. Wheatley’s references contain much useful information and represent a considerable recent advance in understanding.

When flashing occurs, there are two mechanisms by which fine droplets may be formed. The first is due to the flashing process itself, about which little is known. Some experiments and theoretical studies have been done for water, but it is not clear how these can be extrapolated to other materials. However, there is a second mechanism whereby liquid fragmentation can occur. At high speeds, surface stresses cause large droplets to become unstable. The maximum stable drop diameter \( d \), as found from experiment, is given by setting the Weber number \( W \) equal to 20:

\[
W = \frac{v^2 d \rho}{\sigma} = 20
\]

where \( v \) is the velocity of the drop, \( \sigma \) is the coefficient of surface tension and \( \rho \) is the density of air. Using this criterion, Wheatley has shown that the maximum drop sizes for a simulation of Jet 1 (direct tank wall rupture) and Jet 2 (with a 10m pipe of diameter 5cm) are sufficiently small that they would not be expected to fall out before enough air has been entrained to evaporate them. Thus, the observation that little or no rainout takes place in many cases of liquefied ammonia releases has at least a qualitative explanation. However, it is not possible to predict actual drop size distributions.

The entrainment of air into a denser-than-air, high velocity momentum jet containing liquid droplets has been summarized by Wheatley \cite{19}, who noted that, once the initial flashing has taken place (for which he assumes no entrainment), the jet half-angle is initially \( 5^\circ \) \cite{3, 24}, giving an effective entrainment coefficient of about 0.04. This value is about half that usually quoted for entrainment into turbulent, gaseous jets. An explanation can be derived from the entrainment assumptions of Morton, Taylor, and Turner \cite{21}, from whose work it can be deduced that:

\[
\tan \beta = \frac{1}{2} \left( \frac{\rho}{\rho_a} + 1 \right) \tan \beta_a
\]

where \( \beta_a \) is about \( 9^\circ \), \( \rho_a \) is the density of air and \( \rho \) is the density of the jet. Thus, for very dense jets, \( \tan \beta \sim 1/2 \tan \beta_a \). Most measurements have been made on jets that have \( \rho_a \sim \rho \). An ammonia jet with a high content of droplets initially has \( \rho >> \rho_a \) so that a relatively narrow jet is expected.

![Figure 2. Evolution of a flashing ammonia jet.](image-url)
The various stages of evolution of a flashing ammonia jet are shown on Figure 2. Initially, there is a flashing zone (A) in which the width of the jet increases rapidly and liquid ammonia is atomized. As noted above, modelers have to date assumed little entrainment of air at this zone (A) in which the width of the jet increases rapidly. Once enough air has been entrained to evaporate all of the liquid droplets, the jet enters Stage C, a gaseous momentum jet. As dilution continues and the density of the jet decreases, the half angle increases to about 9°. Once enough air has been entrained to slow the jet down so that momentum effects no longer dominate, the plume begins to sink under the influence of gravity (Stage D), and the rate of entrainment will depend in part on the downward velocity. If the plume should fall to the ground during this phase, it will lose its roughly circular shape and slump (Stage D'). At some point, slumping will terminate and the plume height will begin to increase under the action of atmospheric turbulence, although at a rate still influenced by density effects (Stage E). Finally, the plume makes a transition to neutral buoyancy Stage F.

Figure 2 is somewhat idealized. For example, the transition may occur directly from Stage B to Stage D or D'; the orientation of the jet is clearly a key factor. Each of the stages has been studied by various authors; stages A and B have been reviewed above. Ooms and co-authors have developed models that will handle stages C and D, together with a subsequent evolution to stage F of the plume does not touch the ground [22]. There are numerous models that will handle stages D', E, and F. To my knowledge, however, no one has attempted an integrated model of stages A–F. Even though the understanding of the physics and chemistry of all of the stages is not complete, it is sufficient for such a model to be useful.

**Semi-Refrigerated Releases**

The above discussion is tied to the case of fully pressurized storage (e.g., at ~20°C). However, sometimes ammonia is kept semi-refrigerated at about 0°C so that pressures in the vessels are considerably lower than for the fully pressurized systems. In principle, the foregoing discussion should be repeated for the semi-refrigerated case for the modes of release A through D on Figure 1. Considerable differences could arise if there is significant rain-out of liquid droplets at the lower pressure. However, experiments on jets of semi-refrigerated liquid ammonia were done by Fabriken [23] in Holland in 1972 and 1980. With the jet horizontal, 14% of the total release was collected on the ground. This compares with an estimated initial airborne droplet fraction of 90%, so rainout is not significant.

The Crete accident [9] is of some relevance here, since the atmospheric temperature at the time of release was ~15°C and the corresponding pressure inside the rail tanker only ~2 atmospheres. In spite of this, a large, slumping vapor cloud was formed which does not seem to have been any smaller than that expected following the failure of a fully pressurized tank at ~20°C.

Wheatley [20] has analyzed the discharge of semi-refrigerated ammonia via a 10m pipe of diameter 5cm. Using the Weber number criterion outlined above, the maximum stable drop size is predicted to be such that no rainout will occur.

The United Kingdom Health and Safety Executive (HSE) has recently sponsored a series of experiments at the South Bank Polytechnic in London [24] in which a small-scale vessel containing Freon-11 under pressure was pneumatically separated into two halves. The range of pressures studied was 310 to 517 kPa (~3 to 5 atmospheres) and the percentage fill varied from 25 to 85 percent. (For ammonia semi-refrigerated at 0°C, the pressure in the vessel is between 4 and 5 atmospheres.) Bettis, et al. showed that, at 4 to 5 atmospheres, the airborne Freon-11 vapor fraction is 20–25%, the liquid droplet fraction is of the order of 40–60%, and the liquid fraction remaining in the vessel or falling out nearby is in the 20–30% range. Thus, assuming that these results can be extrapolated to the case of ammonia, the majority of the cloud would become airborne with more than enough droplets to lead to the formation of a heavy, slumping cloud. The results of other experiments on flashing liquids at low superheat may be found in Fletcher [25].

The limited evidence available to date suggests that the semi-refrigerated and full pressurized releases will behave in similar fashion, with the exception that a small fraction of the liquid droplets may fall to the ground in the vicinity of the vessel.

**Spillage of Refrigerated Liquid Ammonia onto the Ground**

If a tank containing refrigerated anhydrous ammonia at atmospheric pressure should fail, the liquid will spill onto the ground and evaporate at a rate determined by how rapidly heat can be conducted from the ground into the liquid. (See Figure 1E.) The calculation of the evaporation rate is well understood, for both the ammonia being confined within a bund and spreading in unconfined fashion across the ground [26]. The boiling or heat transfer process is likely to be gentle and sufficient ammonia droplets to cause the resulting vapor cloud to become dense will not be thrown into the air. The plume will be buoyant or passive; its dispersion can be modeled using well-established techniques.

**Spillage of Refrigerated Ammonia onto Water**

When refrigerated ammonia is spilt onto water, a boiling spreading pool is formed on the surface (see Figure 1F). Some of the ammonia dissolves in the water (typically ~60%). This liberates heat of solution, warming the mixing layer. Raj, et al. [27] reported localized temperature rises just beneath the surface of up to 40°C above the ambient water temperature. This liberated heat of solution rapidly evaporated the remaining ammonia. Raj, et al. [27] developed correlations for the prediction of pool size and evaporation rate.

Buoyant plumes were observed in the experiments carried out by Raj, et al., in which up to 130 kg of refrigerated ammonia was spilled onto water in the open air. However, there is evidence that some of the concentration profiles had a maximum at ground level, which is not consistent with the behavior of a buoyant release. For five of the tests, carried out at windspeeds of 5 m/h or less, the dosage peaks were well above ground level, while the peaks were at ground level for those three tests in which the windspeed exceeded 7 m/h. A possible explanation is that the plume was indeed less dense than the surrounding air but that its lift-off was partly or wholly suppressed by the wind-speed-dependent mechanism discussed by Briggs [13]. This is the phenomenon that is often observed with a stubble fire. If there is little wind, the smoke rises into the air. If there is a brisk wind, the smoke may not rise off the ground. Similar suppression of lift-off may also occur if the ammonia is spilled within the turbulent wake of a building. Briggs considered the problem by comparing typical buoyancy-induced velocities (which for both buoyant and dense vapors are proportional to \(\sqrt{ghAp/\rho_L}\) with typical turbulence-induced spreading velocities (which can be taken to be proportional to \(u_c\), the friction velocity). The square of the ratio of these
velocities is the Richardson number \( L \), where:

\[
L = \frac{gh \Delta \rho}{u_p \rho_a}
\]

(3)

\( h \) is the cloud height (i.e. vertical depth), \( \rho_a \) is the density of the air, \( \Delta \rho \) is the density difference between the cloud and the air, and \( g \) is the acceleration due to gravity. If \( L \) is below some critical value, lift-off will be suppressed. The expression for \( L \) shows that it decreases with increasing windspeed so that failure to lift-off at higher windspeeds in the Raj experiments is consistent with Briggs' formulation.

Experimental work by Meroney suggests that a critical value for \( L \) should be about 20 \([28]\). Hall, et al.'s \([39]\) recent work provides other data on lift off.

In general, the modeling of ammonia spills onto water is relatively well understood.

**High Velocity Jet from Refrigerated Containment**

Ammonia may be contained as a refrigerated liquid at its atmospheric boiling point but still under high pressure; for example, it may be subject to a large hydrostatic pressure head. (See Figure 1C.) If such a container were to be breached so as to produce a small hole or crack through which the liquid could emerge as a high velocity jet, it is possible that the jet could be fragmented by an atomization process that could leave some of the droplets airborne and significantly affect the density of the cloud. It is conceivable that the accident reported by MacArthur et al.'s \([25]\) is an example of a heavy vapor cloud that was formed by this means.

Wheatley \([29]\) has performed a theoretical study of the discharge of refrigerated anhydrous ammonia under a 25 meter head through a 10m pipe of diameter 5cm. Using the Weber number criterion discussed above, the maximum stable drop size was predicted to be right on the margin of that required to cause rainout. Wheatley concludes that the degree of vaporization of the drops before they finally settle out will depend on the orientation and height of the outlet above the ground. It may be that, in some cases, a substantial fraction of the droplets (enough to produce a heavier-than-air plume) will be vaporized before they reach the ground. However, a more refined study of the trajectory and rate of vaporization of the drops is necessary in order to make realistic predictions.

**Releases of Anhydrous Ammonia into Moist Air**

Some authors have begun to analyze the mixing of ammonia with moist air \([19, 20, 31]\). In the early stages of dispersion, mixed droplets of water and ammonia appear. The heats of condensation and mixing affect the temperature and density of the cloud. A preliminary comparison \([32]\) with the Desert Tortoise experiments has been carried out using the results of two codes, DEGADIS for heavy vapor dispersion and TRAUMA for the thermodynamic properties of mixtures of ammonia and moist air. However, these simulations were in no sense a test of a fully integrated model. Preliminary comparisons of a newly developed phase change model in the code FEM3 \([33]\) were recently made with ammonia and hydrogen fluoride experiments. These reproduced cloud temperature as a function of downwind distance quite well. However, work remains to be done before such models can be said to be fully validated.

**SUMMARY**

The modes of release for which adequate modeling techniques appear to exist are small hole in the vapor space of a pressurized vessel, catastrophic failure of pressurized vessel, spillage of refrigerated liquid onto the ground, and spillage of refrigerated liquid onto water.

The modes of release for which considerable progress in understanding has been made in recent years are basically those involving the escape of a liquid or two-phase jet from pressurized storage, namely jets 1, 2, and 3 on Figure 1D. There is promise that an integrated model can be developed from existing work. The largest outstanding difficulty seems to be prediction of aerosol size distributions. Thought also needs to be given to criteria for transition between various regimes; e.g., momentum jet to gravitationally dominated plume.

The modes of release for which good modeling does not yet seem possible include an intermediate hole in the vapor space of a pressurized vessel, for which there is difficulty in characterizing the nature of the flow through the orifice, e.g. the ratio of vapor to liquid. For a liquid, flashing jet impinging onto a surface, it is difficult to predict the amount of liquid droplet recovery. For a refrigerated jet driven by a high static head it is difficult to predict the amount of fragmentation.

Good progress has been made in understanding the interaction of ammonia with moist air, although there is some way to go in the development of a validated model that fully integrates dispersion and thermodynamic properties. Finally such limited evidence as there is suggests that semi-refrigerated releases should be treated in the same way as fully pressurized releases.

**PRACTICAL IMPLICATIONS**

It is pertinent to consider the practical implications of the foregoing discussion. It is apparent that the mode of release of ammonia significantly influences the subsequent atmospheric dispersion. Therefore, in examining the risks associated with any facility that handles anhydrous ammonia, careful consideration must be given to the determination of the possible modes of release. There are established techniques of hazard identification that can be used to do this, among them being, for example, the Hazards and Operability Review. A recent survey of these techniques has been published by the Center for Chemical Process Safety \([34]\).

A pertinent example of how important it is to model the release of ammonia in a realistic fashion relates to predictions of how far downwind concentrations exceeding the LC50 will extend. The LC50 is the concentration that will prove fatal to 50% of those exposed to it and is approximately 20,000 ppm(v) for exposures of a few tens of minutes. A recent review \([35]\) of the consequences of about 40 accidental releases of anhydrous ammonia showed that concentrations exceeding the LC50 have never been seen beyond about 200 meters from the source of the spill. Even the Desert Tortoise experiments, which had extremely large release rates of about 100 kg/sec, showed concentrations falling below the LC50 no more than 800 meters from the point of release. By contrast, using the traditional Gaussian model, a release of 100 kg/sec in atmospheric stability class F with a low windspeed of 2 m/sec is predicted to propagate about 2 km downwind before concentrations fall below the LC50. The reason for the difference is that, for flashing liquid releases, the initial flashing and turbulent mixing process causes rapid dilution to the LC50 before the plume has travelled more than a short distance.

Equally important, because there are so many different modes of release, it is not realistic to expect that there will be a dispersion code in the form of a black box that will adequately address all possibilities. On the contrary, dis-
dispersion models must be carefully matched to the mode of release. This observation has some implications for the use of systems that are tied into meteorological data collection systems and are used to make real-time predictions of atmospheric dispersion in the event of an accident. It is unlikely that such a system will have all of the above modes of release programmed into it; indeed, I know of no commercially available system that does cover all of the possibilities. Furthermore, in the event of an accident, there is some question as to whether the information required for the operators of the system to make an informed judgment about the mode of release can be quickly and adequately relayed from the field. It is unlikely that the system operators, who often are not trained as dispersion analysts, will have the background and depth of knowledge to make reliable judgments about the mode of release. It is clear that the complexities that arise from the many possible releases of ammonia mean that real-time dispersion models should be used with caution and a degree of scepticism during actual accidental releases.

Once a release has occurred, there may at first be some doubt about the causes and progression of the accident. The mechanism of the release may not always be self-evident. It may be necessary retrospectively to evaluate several candidate modes of release, coupled with observations of damage, in order fully to understand what has taken place.

**LITERATURE CITED**


DISCUSSION

J. BLANKEN, DSM Fertilizers, Ijmuiden, The Netherlands: In your paper, you mentioned that, in the case of spillage of semirefrigerated liquid ammonia onto the ground, the plume will be buoyant or passive, and its dispersion can be modeled using well-established techniques. I have some difficulty with that “buoyant” or “passive.” I do agree that, immediately after the semirefrigerated liquid ammonia touches the ground, you will have a buoyant plume but then the pool will tend to be in a stationary situation. The temperature will become approximately -50°C, the air above that pool will be adiabatically saturated with ammonia, and then there will be a blanket of cold air with condensed water vapor moving over the area around the pool.

It is illustrated best by the only incident I know of: a large spill of cold liquid ammonia over the ground which was presented at this symposium in 1971. The paper discussed a Chicago Bridge tank with an overflow device. The overflow operated and it spilled over the ground, and there was a descriptive picture of a tremendous blanket. Maybe you are interested in a simple experiment we did before we constructed concrete walls around our atmospheric storage tanks. We wanted to check ourselves that the concrete would withstand the impact of the temperature difference. We did it a long time ago. We took a bucket, just an ordinary galvanized bucket; we filled it 50% with ammonia, put a thermometer in, measured the temperature, and then in no time we had -50°C. We dumped some concrete in it and, after some time, we took it out again. Nothing happened to the concrete, but the temperature was -50°C. And that’s what you get in a pool after you have reached adiabatic conditions, and then you get a heavier-than-air plume going over the pool.

G.D. KAISER, Science Applications International, McLean, VA: Yes, Mr. Blanken, of course, this illustrates the dangers of trying to generalize in a situation where many, many phenomena are important. I can’t cover every situation in the short time that I have. I would like to make one comment. I think that your remark about the release in which the ammonia was driven out of some kind of overflow relates more likely to a case driven by a high-static head, in which fragmentation by hydrodynamic forces might have contributed to the formation of liquid droplets which in turn contributed to the observed “blanket over the ground.” Pure ammonia vapor at -50°C, when evaporating from a pool and mixing with air, is buoyant.

D. CINDRIC, The M.W. Kellog Company, Houston, TX: The modeling of a buoyant plume is developed fairly well. In fact, the U.S. EPA has even issued guidelines on how to model buoyant plumes. But, the dense gas model is much more complicated and the EPA has not endorsed a method for doing that yet. In your opinion, what’s the best available model for dense gas dispersion?

KAISER: I am not going to answer that question. There are several models around, many of which are equipped with adequate features. DEGADIS is an example which is a basically U.S.-Government-Agency-sponsored code. HEGADAS is another which I guess is a Shell Oil model. I’ll put in a plug for my own models, the DENZE Suite of Codes, which was developed for HSE in the U.K. They also contain most of the features that you need. I don’t want people to think that I am ruling the other models out. None of the models is perfect, but many of them do an adequate job.

E.D. CHIKHLIWALA, Chemodynamics, Westlake Village, CA: Can you explain your statement that semirefrigerated releases behaved the same as pressurized releases? I would have thought that the flashing fraction differentiates them, resulting in different turbulent characteristics. Would you explain?

KAISER: Experiments have been done in the U.K., sponsored by the Health Safety Executive, looking at the amount of liquid droplets remaining airborne as a function of pressure in the vessel or, equivalently, the temperature above the boiling point. The experiments showed that, for the degree of superheat in a semirefrigerated vessel with pressures of 4 or 5 atm, the majority of the contents will become airborne when you look at sudden releases. Maybe you will get 20% dropping on the ground. The situation is quite similar to the fully-pressurized case.

There was a railway accident at Crete in Nebraska 10 or 20 years ago, in which the outside temperature was well below zero, so that the ammonia temperature may have been only 20° above its boiling point. But all of the descriptions that you see of the accident suggest that you got the big puff of heavy vapor, which spread to about the same extent as you get for fully-pressurized vapor clouds.

My comment is based on these two observations about the semirefrigerated releases.

CHIKHLIWALA: Wouldn’t there be a kind of gradual change in the phenomena when you go from pressurized to fully-refrigerated?

KAISER: Yes. My point is that 0°C is closer to the fully-pressurized case than it is to the fully-refrigerated case. In other words, you haven’t really reached the
region of transition at that point. You need to go a bit lower in temperature.

**R.D. WILLIAMS, BASF Chemicals Limited, Middlesbrough, England:** As a tank operator, has anyone ever asked you how you design the nozzle which makes it easier or faster to recommission or commission an ammonia tank using your technical information?

**KAISER:** I'm not sure I understand the question.

**WILLIAMS:** You have to displace nitrogen or air depending on your technique with ammonia, and there have been discussions about densities and the length of time it takes and one or two other phenomena. I was just curious as to whether anyone had asked you how to design a nozzle, or is there some mileage in designing a nozzle to get a plugflow using your data.

**KAISER:** That is a question which I have never considered, so I'm afraid I cannot answer that.

**BLANKEN:** The question as I understand it is that you would like to commission a tank filled with air and to replace the air with ammonia. Articles have been published 10 or 15 years ago about this. When you commission the tank, you have to be careful in making the connection for vaporized ammonia at the top of the tank and you should go down the tank at such a speed that you replace all the air in about 36 hours. You should vent from the bottom of the tank through a hose running up the stairway or something like that, and then you get a front moving through the tank and you will go from zero ammonia to 100% ammonia in about 2 or 3 hours. Does that answer your question?

**WILLIAMS:** Yes, I understand that, but nozzles that I've seen don't ever appear to have a scientific basis for their design. I wondered if, from your information, there was now a better way of locating nozzles, designing the spray nozzle, and making life perhaps faster and simpler.

**KAISER:** I'll say I'll have to pass on that question.

**J. CURTIN, Irish Fertiliser Industries, Cobh, Ireland:** The essence of your paper is that there are various models and that some are more satisfactory at this stage than others. At the present time in Europe, we have to prepare safety cases to comply with EEC Legislation and an important part of these safety cases will have to cover certain incidents and types of dispersion which occur. Are there models available which have been approved by certain regulatory bodies in the U.S.? This type of information would obviously be of some relevance in preparing our own safety cases.

**KAISER:** To my knowledge, no heavy-vapor dispersion models have been approved by U.S. Government Agencies or State Agencies. They recognize that the developing status of these models, I think, makes it unwise to put money into a code at this stage.

**CURTIN:** Thank you.