

## PRODUCTION OF DENSE GAS MIXTURES FROM AMMONIA RELEASES — A REVIEW

R.F. GRIFFITHS

*Pollution Research Unit, University of Manchester Institute of Science and Technology,  
Manchester, M60 1QD (Gt. Britain)*

and G.D. KAISER

*NUS Corporation, Rockville, MD 20850 (U.S.A.)*

(Received September 10, 1981; accepted November 10, 1981)

### Summary

Ammonia is a material of special importance in hazard control, because of its toxicity and its very widespread use. An additional factor is its ability to form denser-than-air mixtures on release to the atmosphere, in spite of its low molecular weight relative to that of air. Observational and theoretical evidence is reviewed that demonstrates the formation of such mixtures. It is shown that the combination of factors determining the density of the mixture is highly dependent on the mode of containment and the details of the mode of containment-failure; the physical properties of ammonia and the meteorological variables also have an important influence. Suggestions are made for investigations that are needed in order to improve the confidence with which a given release can be assigned to a particular density regime. A compilation of accidental releases of ammonia is included.

---

### Introduction

This paper concentrates on issues in the modelling of accidental releases of ammonia to the atmosphere, and is intended as a review of relevant work from various sources, including material reported elsewhere by the authors and their colleagues [1–7].

Although some of this work is readily available in journal publications, much of it is to be found only in less-widely distributed reports, as referenced.

It is not immediately apparent that ammonia can, in some circumstances, be part of a denser-than-air mixture, since its molecular weight is  $\sim 17$ , compared with  $\sim 29$  for air, and the vapour density at the boiling point temperature ( $\sim -33^\circ\text{C}$ ) at normal atmospheric pressure is  $\sim 0.9\text{ kg m}^{-3}$ , compared with  $\sim 1.2\text{ kg m}^{-3}$  for ambient air at  $20^\circ\text{C}$ . However, there is a substantial body of evidence demonstrating that ammonia and air can form mixtures that are denser than the ambient air. This evidence is to be found in a number of accident reports [8–14], and in the report of field experiments carried out on controlled releases from pressurized containers [16]; it is also summarized in other reports [3,4,7].

Ammonia is one of the most widely used materials of current concern in hazard control. The principal use is in the manufacture of nitrogenous fertilisers, and as a fertiliser for direct application to the soil. It is also used in the manufacture of explosives, in the textile and fibre industries, in metal treatment, as a corrosion inhibitor, in water and aqueous effluent treatment, and as the working fluid in some refrigeration systems. It can be liquefied by cooling and/or pressurization, and is commonly transported overland as a liquid in pressurized ambient-temperature road or rail tankers containing some tens of tonnes. It is also shipped in purpose-built barges and ocean-going vessels, usually as a fully-refrigerated liquid, but sometimes as a liquid under pressure. Pipeline systems exist in which pressurized ammonia is pumped over distances of several hundred miles. Static storage of large quantities (thousands of tonnes) is usually in fully refrigerated tanks, but some systems utilise a partially refrigerated containment at about 0°C in which there is an over-pressure of about 4 atmospheres. Pressurized ambient-temperature tanks are also in use for static storage. The vapour pressure at 20°C is about 9 atmospheres.

Ammonia-air mixtures are combustible in the concentration range 15.5% to 27% by volume [29], but it is the toxic properties that are of primary concern in hazard control; ammonia is listed as a non-flammable gas in many hazard codes [30,31].

Ammonia is an irritant with very damaging effects if ingested or inhaled. The damage resulting from inhalation depends on the concentration and the duration of exposure. Concentrations of a few hundred p.p.m. (*v/v*) cause irritation to the eyes and mucous membranes, whilst exposures at a few thousand p.p.m. (*v/v*) can be lethal after a few minutes, due to respiratory failure [32,33]. There have been a number of accidental releases of significant quantities over the last thirty years, the current frequency being about one per year. Table 1 lists incidents compiled from various sources [3,8-14,34-42].

### Density of ammonia-air mixtures

The observations referred to above concerning the occurrence of dense mixtures of ammonia and air led Haddock and Williams [1] to examine the problem theoretically. They considered the possible chemical and physical interactions of ammonia with the components of the atmosphere and concluded that under some combinations of circumstances dense mixtures could be formed. The aspects of their treatment dealing with the density of such mixtures can be summarized as below. Throughout this discussion the term ambient air is used as a convenient shorthand for air at a temperature of ~20°C and a pressure of 1 atmosphere.

When anhydrous ammonia escapes to the atmosphere, it forms a mixture which may contain any or all of the following:

- (i) Ammonia vapour.
- (ii) Fine droplets of liquid ammonia (pure or aqueous).

TABLE 1

## List of ammonia releases

Year	Place	Quantity (tonnes)	Source	Injured	Dead
1952	?	15	ST	20	15
1959	Ube, Japan	—	R(Ex)	40	11
1961	Creve Coeur, Illinois	350	Barge	—	—
1962	Brandenburg, Kentucky	—	R(Ex)	19	0
1965	Pasadena, Texas	—	R(Ex)	3	2
1968	Lievin, France	19	RdT	15	6
1969	Crete, Nebraska	90	RlyT	53	9
1969	Cumming, Iowa	—	—	—	0
1970	Belle, West Virginia	75	RlyT	30	0
1970	Blair, Nebraska	160	ST	3	0
1971	Floral, Arkansas	600	PL	0	0
1971	Texas City, Texas	—	PW	2	—
1973	Potchefstroom, South Africa	38	ST	65	18
1973	Conway/McPherson, Kansas	280	PL	2	0
1974	Hutchinson, Kansas	350	PL	4	0
1975	Texas City, Texas	50	PL	—	0
1976	Glen Ellyn, Illinois	52	RlyT	15	0
1976	Landskrona, Sweden	180	Ship to ST	—	2
1976	Enid, Oklahoma	500	PL	—	0
1976	Houston, Texas	19	RdT	200	6
1977	Mexico	—	—	102	2
1977	Cartagena, Columbia	—	—	22	30
1977	Pensacola, Florida	40	RlyT	46	2
1979	Vilvorde, Belgium	8	Rly or RdT	—	—

## Key

ST	— Storage Tank
R	— Reactor
Ex	— Explosion
RdT	— Road Tanker
RlyT	— Railway Tankcar
PL	— Pipeline
Cyl	— Cylinder
PW	— Pipework, including loading lines.
?	— Information uncertain
—	— Indicates lack of information

## (iii) Air (with or without water vapour or condensed water droplets).

For the general case, with air, ammonia vapour and droplets mixed together, the possible range of densities is displayed in Figs. 1 and 2. The interpretation of Fig. 1 is that the density is that of the mixture produced by adding dry ambient air to a mass of pure ammonia at  $-33^{\circ}\text{C}$ , of which a fraction  $F$  is in the form of pure liquid droplets and the residual fraction  $(1 - F)$  is pure vapour. The admixture of air causes evaporation of the ammonia droplets,

and the resultant cooling lowers the temperature of the mixture. The interpretation of Fig. 2 is the same except that the air is assumed to be initially saturated with water vapour. The following deductions may be made:

- (i) If ambient air, wet or dry, is mixed with pure ammonia vapour, the mixture is always less dense than the surrounding air.
- (ii) There is a critical value for the initial liquid fraction,  $F$ , between 4%

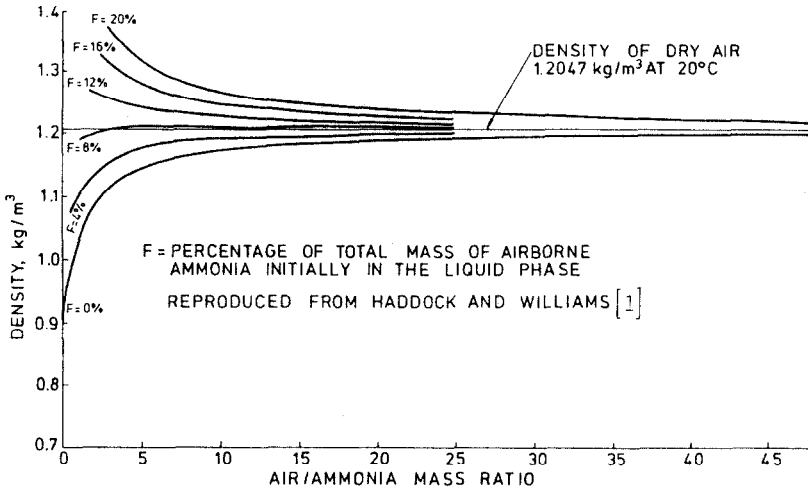


Fig. 1. Density of ammonia cloud initially containing some liquid ammonia as it is diluted with dry air.

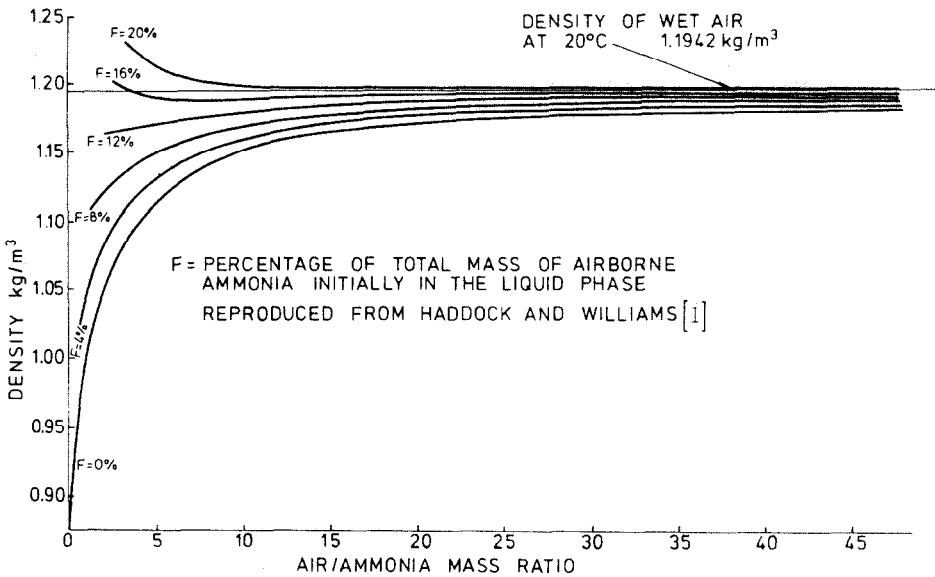


Fig. 2. Density of ammonia cloud initially containing some liquid ammonia as it is diluted with wet air.

and 8% of the total airborne mass of ammonia for air at 20°C such that, if  $F$  is less than this value, then the cloud will remain less dense than the surrounding air, regardless of the humidity.

- (iii) There is a second value of  $F$ , between 16% and 20%, such that, if the fraction exceeds this value, the cloud will become denser-than-air at low dilution and will remain so throughout the subsequent dilution process regardless of the humidity of the air.
- (iv) Between these two critical values of  $F$  the density relative to air will be determined by the humidity of the air as well as by the dilution, lower values of humidity being associated with higher cloud densities.

It is apparent from this that the key to the understanding of the density of a mixture of ammonia and air lies in the answers to two questions, namely:

- (i) What fraction of the airborne ammonia is entrained as droplets that are fine enough not to fall to the ground?
- (ii) How much air is entrained?

The answers to these questions depend on the way in which the ammonia escapes from its containment. A thorough analysis of the conceivable modes of release is given elsewhere [5] and is summarized briefly here (see also [7] and [15]).

### Modes of release of ammonia

#### *Pressurized tank, small hole in vapour space*

In this context, the definition of a 'small' hole is that  $R = a_h/A_s \ll 1$ , where  $a_h$  is the area of the hole and  $A_s$  is the area of the liquid surface. For anhydrous ammonia, stored in a tank at ambient temperature, pure vapour is likely to emerge at sonic velocities. The plume will be buoyant and its behaviour can be treated by using standard plume rise modelling.

#### *Pressurized tank, large hole in vapour 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. 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 [16]. The remaining 80% stays as a liquid at the boiling point, -33°C, 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 [17] and propylene [18].

During the bulk boiling and expansion, considerable turbulence is generated and air is entrained, perhaps of the order of ten kg of air for every kg of ammonia that is initially thrown into the air [6]. For releases of this kind it is clear that since the liquid fraction (80%) greatly exceeds the critical value of 16% to 20% referred to in Figs. 1 and 2, the air-ammonia mixture is certain to be denser-than-air.

### *Pressurized tank — intermediate hole in vapour space*

There must be a range of intermediate hole sizes over which the resulting ammonia—air mixture changes from being buoyant to being denser-than-air. In the nuclear field, experimental work on the depressurization of steam liquefied under pressure has shown that a hole with  $R \sim 0.01$  qualifies as large since the bulk of the contents of the experimental vessel escaped when an orifice of that size was opened [19]. For the time being, however, it is not possible to treat the ‘intermediate’ case since the size of hole that qualifies as such for ammonia is not known.

### *Holes in the liquid space of a pressurized container*

There are several different ways in which it is conceivable that liquid could escape from a pressurized vessel through holes in the wall, or through pipes. If the hole is in the wall of the vessel itself it is reasonable to expect that, at least at first, the jet consists of ‘unflashed’ liquid. The liquid will then ‘flash’ causing the jet to expand rapidly — blowdown experiments with steam liquefied under pressure have shown that the half-angle can sometimes exceed  $90^\circ$ .

There appear to be little data or theoretical work on the entrainment of air into such jets, so that this remains an area within which further research is required. If the jet emerges from a long pipe there is the possibility that vapour will flash within the pipe so that a two-phase jet will emerge into the atmosphere. In this case the jet does not flash completely in the pipe — there is still a pressure drop as it emerges into the atmosphere and further flashing then takes place. From experiments such as those carried out by Resplandy [16] there is no doubt that, when a jet emerges from the liquid space in a pressurized container, the mixture of air, ammonia vapour and ammonia droplets that is found is always denser than the surrounding atmosphere. This is true even if the jet plays onto a surface and some of the droplets are removed from it and collect as a pool. The subsequent evaporation of this pool is not likely to produce a denser-than-air vapour, however, as is explained below.

### *Spillage of refrigerated liquid*

If a tank containing refrigerated anhydrous ammonia at atmospheric pressure should fail, the liquid will spill onto the ground and evaporate. Except in the very early stages of such a spill the boiling or heat transfer process is likely to be gentle and it seems unlikely that sufficient liquid ammonia droplets will be thrown into the air to cause the resulting vapour cloud to become dense; it will therefore behave in a buoyant or perhaps passive fashion. When refrigerated ammonia is spilt onto water, a boiling, spreading pool is formed on the surface. Some of the ammonia dissolves in the water (typically  $\sim 60\%$ , but experimental values range from 30% to 98% [21]). This liberates heat of solution, warming the mixing layer. Raj et al. [21] reported localised temperature rises just beneath the surface of up to  $40^\circ\text{C}$

above the ambient water temperature. The picture is then a surface pool of ammonia at its boiling point of  $-33^{\circ}\text{C}$ , and the bulk of the water below remaining at its ambient temperature (typically  $10^{\circ}\text{C}$ ), with a warm mixing layer sandwiched between the two. It is clear that heat cannot then travel from the bulk of the water (as for a boiling pool of LNG) since there is an adverse thermal gradient, and it follows that the heat required to boil-off the remainder of the ammonia must be supplied predominantly by the release of heat of solution. One might well expect that buoyant ammonia vapour would be evolved by this boiling process. Buoyant plumes were observed in experiments carried out by Raj et al. [21] in which up to 130 kg of refrigerated ammonia was spilled onto water in the open air; however, there appears to be evidence contained within the Raj report that, for some of the spills, the dosage profiles had a maximum at ground level, which is not consistent with the behaviour of a buoyant release. For five of the tests, carried out at wind-speeds of 5 m.p.h. or less, the dosage peaks are well above ground level, while the peaks are at ground level for those three tests in which the windspeed exceeded 7 m.p.h.

Two possible explanations for this behaviour have been advanced [5]. First, since the boiling on water is vigorous, it is therefore plausible that liquid ammonia droplets could be thrown into the air by the bubbles of vapour bursting at the surface. If the fraction,  $F$ , of the ammonia released to the air that is in the form of droplets were to exceed the lower critical value identified by Haddock and Williams [1], which lies between 4% and 8%, then that would be sufficient to produce a dense release in some cases. In forthcoming large scale experiments with up to 6 tonnes of refrigerated ammonia, to be carried out at China Lake [22], this possibility will be investigated.

A second explanation, and one which is the more likely in view of the observation that the plumes in the Raj experiments were buoyant at low wind-speeds, but perhaps not at the higher ones, is that the plume was 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 [23]. 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 vapours are proportional to  $[gh\Delta\rho/\rho_a]^{1/2}$ ) with typical turbulence-induced spreading velocities (which can be taken to be proportional to  $U_*$ ). The square of the ratio of these velocities is the Richardson number,  $L$ , where

$$L = gh\Delta\rho/U_*^2\rho_a \quad (1)$$

and  $h$  is the cloud height (i.e. its vertical depth),  $\rho_a$  is the air density,  $\Delta\rho$  the density difference between the cloud and the air,  $g$  is the acceleration due to gravity and  $U_*$  is the friction velocity. Briggs estimated that lift-off would be

suppressed if  $L < 2$  for a continuous plume, and similarly if  $L < 2.5$  for a puff release, with a large factor of uncertainty (of about 4) in the critical value for  $L$ . If one substitutes for  $U_*$  using the well-known expression for windspeed  $\bar{U}(z)$  a function of height  $z$ ,

$$\bar{U}(z) = U_* \ln(Z/Z_0)/k \quad (2)$$

where  $k$  is von Karman's constant and  $Z_0$  is the meteorological roughness length, it follows that

$$L = \frac{gh\Delta\rho}{\rho_a} [\ln(Z/Z_0)/k\bar{U}(z)]^2 \quad (3)$$

from which it is readily seen that low values of  $L$  are associated with high windspeeds and large values of  $Z_0$ , i.e. the higher the windspeed and the rougher the terrain, the more likely is lift-off to be suppressed. The apparent division into two regimes in the Raj experiments is consistent with Briggs' proposals for the critical value of  $L$ . However, more recent experimental work suggests that, if there is indeed a single critical value, it should be more like 20 rather than 2. Meroney [43] carried out experiments in a wind tunnel and concluded that for continuous point sources the critical value of  $L$  was in the range 9 to 27, well outside of the range suggested by Briggs (0.5 to 8). The most recent experimental work of which the authors are aware has been carried out in the Warren Spring Laboratory wind tunnel [28]. Helium was emitted into the turbulent wake of buildings which were in the form of rectangular parallelepipeds, and some insight into the behaviour of buoyant plumes in a building wake was obtained. Clearly there is more experimental work to be done before this phenomenon can be treated with any reasonable accuracy, but it is an important problem in many hazard studies, for both positively buoyant and dense releases.

Finally, 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. 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 [14] is an example of a heavy vapour cloud that was formed by this means.

### Live issues in ammonia dispersion modelling

Refs. [2,4,5 and 7] discuss how the dispersion of ammonia accidentally released into the atmosphere can be modelled in the light of the discussed phenomena. As is shown in [4] the consequences of the catastrophic failure of a vessel containing ammonia liquefied under pressure can be predicted



quite successfully. Rather than review this, however, it is pertinent to focus on those issues that make the modelling of ammonia dispersion difficult and could repay further research. The following list is not meant to be exhaustive:

- (i) The initial entrainment of air into a flashing ammonia puff and the 'ten times' rule of thumb.
- (ii) The entrainment of air into flashing jets.
- (iii) Superheat.
- (iv) Concentration profiles in an ammonia puff or plume.
- (v) Plumes in building wakes.
- (vi) The influence of surface roughness elements.
- (vii) Dry deposition.

The following discussion is focussed on ammonia, but much of it is relevant to other materials.

*Initial entrainment of air into a flashing ammonia 'puff'*

In ref. [2] calculations were described for a release of 20 tonnes of anhydrous ammonia from pressurized containment. In order to define a source cylinder for the gravitational slumping calculations, it was assumed that the initial pressure-energy driven phase entrained of the order of ten times as much air by mass as ammonia. This rule of thumb was justified by reference to the observed dimensions of an ammonia cloud following the accidental catastrophic failure of a pressurized storage vessel at Potchefstroom, South Africa [10]. This assumption has been quite successful in a number of applications to ammonia releases [4,7], but it remains a rule of thumb. Ref. [6] contains an examination of the transition from the pressure-driven to the gravity-driven phase following the catastrophic failure of a vessel containing a gas liquefied under pressure. From work reported in [6] it is possible to prove by dimensional arguments (see Appendix) that

$$M_a \propto M_g^{3/4} (1 - \rho_a/\rho_g)^{-9/4} \quad (4)$$

where  $M_a$  is the mass of air entrained at the time that the transition to gravitational slumping takes place,  $M_g$  is the mass of material released from the pressurized container and  $\rho_a$  and  $\rho_g$  are the densities of air and the released material respectively. For a given value of  $M_a$ , but for materials with  $\rho_a/\rho_g = 0.9$  and  $\rho_a/\rho_g = 0.5$ , the predicted values of  $M_a$  can vary by an order of magnitude or more; the denser the released material, the smaller the value of  $M_a$ .

It is difficult to relate the above observation to ammonia, for which, as has been seen, denser-than-air effects are due to low temperatures rather than the initial density of the released ammonia. However, the quantitative observation may be made that the density of ammonia-air mixtures is not likely to exceed 1.2 times that of air. Hence, for other materials such as propylene, with density ratio 1.88, it is to be expected that, assuming that the 'ten times' rule of thumb is accurate for ammonia, a similar rule of thumb would predict the entrainment of considerably less air than  $10 \times M_g$  at the transition to gravitational slumping. If more quantitative observations are to be made, there

is a need to refine the work of ref. [6] to take temperature effects into account and to include material-specific properties that could lead to the calculation of the coefficient of proportionality in eqn. (4).

#### *The entrainment of air into 'flashing' jets*

As has already been mentioned, there appears to be no published work on the entrainment of air into jets that emerge into the atmosphere as unflashed liquid. For the case of two-phase mixtures in thermodynamic equilibrium, there have been some measurements taken with water sprays and McQuaid [24] has used dimensional analysis to obtain simple formulae for predicting how much air is entrained into bounded axisymmetric sprays. For coarse sprays, the rate of entrainment of air is described by an expression derived by considering entrainment into the wake of individual droplets, while for fine sprays it is found that there is increasing interaction between the wakes of individual droplets so that the whole system behaves as would a continuous jet. There appears to be no published theoretical or experimental work on how such predictions should be modified when the spray in question contains liquid with a boiling point well below that of the entrained air; intuitively, it is to be expected that evaporation of the liquid will enhance the rate of expansion of the plume, generate additional turbulence and, perhaps, cause relatively rapid dilution.

#### *Superheat*

One of the uncertainties associated with the prediction of the consequences of the failure of a pressurized vessel is what degree of superheat is required to ensure that the bulk of the liquid fraction escapes from the tank as droplets that are sufficiently fine to remain airborne. Experiments under way at HSE Sheffield, using Freons with just a few degrees of superheat, produce droplets which are seen to fall [20]. Some ammonia vessels are kept semi-refrigerated at about 0°C, which is about thirty degrees of superheat. The Crete accident [11] is of some relevance here, since the atmospheric temperature at the time of the release was -15°C and the corresponding pressure inside the tank only ~2 atm. In spite of this a large, slumping vapour 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. The uncertainties in the description of the consequences of this release are so great, however, that this point cannot be taken as having been proved conclusively. Nonetheless, it appears that caution is advisable as there is no evidence here to support the contention that the total mass of ammonia becoming airborne from a semi-refrigerated tank is smaller than that from a fully pressurized tank. Equivalently, it is not safe to assume that the consequences of the sudden failure of a pressurized tank kept at a relatively low temperature will be less severe than those due to the failure of a pressurized vessel at a higher (ambient) temperature.

### *Concentration profiles in an ammonia puff or plume*

Relatively little attention has been devoted to this problem. Most authors make the assumption that the concentration through the plume or puff is uniform, at least while gravitational slumping predominates. Zeman [25] has carried out some theoretical work in support of this assumption; he argues that, for plumes or puffs that are much colder than the ground, convective turbulence will be generated and will be sufficiently vigorous to ensure good mixing throughout the depth of the plume, with a sharp gradient at the top. The question of what is the concentration profile above this region, within which the bulk of the dense vapour is contained and is uniformly mixed, has never been satisfactorily answered. It is, however, of considerable importance, in the case of a dense, pancake-like cloud of toxic gas flowing around buildings. It may be necessary to predict the concentration of toxic vapour at an elevated air intake, for example. Havens [26] has developed a simple model in which a Gaussian tail is superimposed on a slab model of heavy vapour dispersion, but accurate predictions of the concentration profile above a slumping vapour cloud are not yet possible.

### *Dense plumes in building wakes*

For a passive plume or puff emitted into the turbulent wake of a building, there exist methods with which it is possible to estimate the initial dilution that may occur due to entrained turbulence within the wake, and the subsequent rate at which the material escapes from the wake and travels downwind. Ref. [27] describes such methods, which are summarised in [5]. If the emitted plume is dense, however, it could successfully resist the attempts of turbulence to mix it throughout the building wake. To the authors' knowledge, there is little work current in the literature which has anything to say about dense plumes in building wakes. Considerations similar to those discussed above dealing with the suppression of lift-off ought to apply to dense plumes and experiments such as those described in [28] should be carried out for heavy vapours.

### *The influence of surface roughness elements*

If a liquid such as refrigerated anhydrous ammonia is spilled onto rough terrain it may well evaporate at such a rate that the depth of the vapour cloud so formed is less than the height of typical roughness elements, such as stones or shrubs. For other materials, with boiling points near the ambient temperature of the ground, the problem is even more acute because adequate methods of predicting the rate of evaporation of such materials, which is dominated by the wind, are not available for liquid pools with depths that are less than the height of typical roughness elements. In any event, the dispersion of dense vapours in pancake-shaped plumes that may initially be so thin that the surface roughness elements rise above them is not understood. This is a problem encountered in attempting to predict the consequences of the spillage of many toxic materials.

### *Dry deposition*

Once a heavy vapour cloud has slumped, it presents a large surface area to the ground. It may be hypothesized that, for a reactive gas such as ammonia, the effective dry deposition velocity could be quite high. As a result, the cloud could be rapidly depleted as it travels downwind and predicted hazard ranges might be much reduced. To the authors' knowledge, however, this possibility has not been examined quantitatively. It would be a worthwhile exercise.

### **Conclusions**

The dispersion behaviour of ammonia releases is complicated by factors arising from the properties of the material, the manner of storage and the characteristics of the failure leading to the release. Mixtures that are denser than air may be formed under a variety of conditions, some of which are well defined and demonstrated. However, in many cases further investigation is called for in order to improve the confidence with which one can assign a release to a particular category of dispersion behaviour.

### **Acknowledgement**

The authors are grateful to the United Kingdom Atomic Energy Authority for permission to reproduce Figs. 1 and 2.

### **Appendix, by G.D. Kaiser**

#### *Proof of equation (4)*

The paper of Maurer et al. [18] provides the following picture of the sequence of events that follows the bursting of a cylinder containing propylene liquefied under pressure. Initially, there is vigorous bulk boiling and between 50% and 65% of the material vaporizes. The remainder is thrown into the air as fine liquid droplets. This flash expansion process is over extremely quickly. It takes place with a constant expansion velocity for a time  $0.001 V_g^{1/3}$  sec, where  $V_g$  is twice the volume of propylene released, measured at ambient temperature and pressure, and there is little or no initial entrainment of air, ( $V_g$ , and the mass released,  $M_g$ , are introduced for scaling purposes). It leaves a hemispherical vapour/droplet mixture in a state of vigorous turbulence, which causes the entrainment of ambient air. As a consequence, the residual droplets evaporate. This sequence of events is basically that described earlier in this paper for catastrophic failure of a vessel containing ammonia liquefied under pressure.

At this stage the rate of growth of the cloud is dominated by the action of its own turbulence. There is a central, well-mixed core of uniform concentration  $C_g$  containing about 50% of the initially released propylene vapour, where

$$C_g = 0.0478 V_g / (4\bar{E}t)^{3/2} \quad (A1)$$

Here  $t$  is time and  $\bar{E}$  is a mean turbulent diffusion coefficient which has been parametrized empirically. The radius of the central core is given by

$$r_g = 1.36 (4\bar{E}t)^{1/2} \quad (\text{A2})$$

Outside  $r_g$  there is a concentration 'tail',  $C$ , where

$$C = C_g \exp\{1.85(1 - (r/r_g)^2)\} \quad (\text{A3})$$

and  $r$  is the radius. The form for  $\bar{E}$  is

$$\bar{E} = 0.75 V_g^{1/3} (t/V_g^{1/3})^{-1/4} \quad (\text{A4})$$

Equations (A1) to (A4) are deduced from experimental observation on tanks containing 0.124, 0.420, 1.95, 6.55, 15.6 and 454 kg of propylene. The relationship  $\bar{E} \propto t^{-1/4}$  is universal and stems from the use of free turbulence theory (i.e. turbulence theory in the absence of walls). The coefficient of proportionality, however, is a function of such quantities as the density, the kinematic viscosity, the mass of vapour in the central core, and the initial pressure.

From eqns. (A1) to (A4) it may readily be shown that

$$\frac{dr_g}{dt} = 1.02 M_g^{5/24} \rho_g^{-5/24} t^{-5/8} \quad (\text{A5})$$

and

$$r_g \propto M_g^{5/24} \rho_g^{-5/24} t^{3/8} \quad (\text{A6})$$

As the turbulence generated during the flash expansion dies away, there will be a transition to gravitational slumping, assuming that  $\rho_g > \rho_a$ . As is well known, the rate of growth of the radius of a slumping cylinder may be well described by a liquid column analogy:

$$\frac{dr}{dt} = K \{gh(\rho_g - \rho_a)/\rho_a\}^{1/2} \quad (\text{A7})$$

(c.f. eqn. (1)), where  $g$  is the acceleration due to gravity,  $h$  is the height of the cylinder and  $K$  is a constant which is often taken to be unity.

In order to determine when the transition to gravitational slumping will take place, it is appropriate to consider the dimensionless combination\*:

$$L = gh\rho_g(1 - \rho_a/\rho_g)/\rho_a \left(\frac{dr_g}{dt}\right)^2 \quad (\text{A8})$$

which is a Richardson number, and is the ratio of the square of the gravitational slumping velocity and the square of rate of growth of the radius during the turbulent expansion (pressure-energy) phase. The assumption that temperature effects may be neglected has been made. It is to be expected that gravitational slumping will be important if  $L \gg 1$  and that it will be negligible

\*It is recognized that this is not the only dimensionless combination.

if  $L \ll 1$ . Assuming that  $h \sim r$  during the pressure—energy expansion, it may be shown that, when  $L = 1$ ,

$$t \propto M_g^{-1/3} \rho_g^{-5/3} \rho_a^2 (1 - \rho_a/\rho_g)^{-2} \quad (\text{A9})$$

where  $t$  is now an estimate of the time of transition to gravitational slumping. Inserting this expression for  $t$  into eqn. (A6) and making use of the fact that  $M_a$ , the amount of air entrained, is given by

$$M_a = \left[ (2\pi r_g^3/3) - (V_g/2) \right] \rho_a \quad (\text{A10})$$

it is easy to show that

$$M_a = C_1 M_g^{1/4} (1 - \rho_a/\rho_g)^{-9/4} - (V_g \rho_a/2) \quad (\text{A11})$$

from which eqn. (4) follows. The  $V_g \rho_a/2$  has been omitted from eqn. (4); if it is included, it reinforces the density effect discussed in the text immediately after eqn. (4).

## References

- 1 S.R. Haddock and R.J. Williams, The density of an ammonia cloud in the early stages of atmospheric dispersion, United Kingdom Atomic Energy Authority Report SRD R103, 1978; also *J. Chem. Tech. Biotechnol.*, 29 (1979) 655–672.
- 2 G.D. Kaiser and B.C. Walker, Releases of anhydrous ammonia from pressurized containers — The importance of denser-than-air mixtures, *Atm. Env.*, 12 (1978) 2289–2300.
- 3 R.F. Griffiths, Observations of non-buoyant behavior of ammonia following accidental discharges to the atmosphere, Published as an Annex entitled Ammonia Release Incidents to Appendix 4 of Canvey; an investigation of potential hazards from operations in the Canvey Island/Thurrock Area, HMSO, London, 1978.
- 4 G.D. Kaiser, Examples of the successful application of a simple model for the atmospheric dispersion of dense, cold vapours to the accidental release of anhydrous ammonia from pressurized containers, UKAEA Report SRD R150, 1979.
- 5 R.F. Griffiths and G.D. Kaiser, The accidental release of anhydrous ammonia to the atmosphere — A systematic study of factors in influencing cloud density and dispersion, United Kingdom Atomic Energy Authority Report SRD R154, 1979. A shortened version of this paper was presented at the 73rd Annual Meeting of the Air Pollution Control Association, Montreal, Canada, June 22–27, 1980 for publication in *J. of the Air Pollution Control Association*.
- 6 S.F. Jagger and G.D. Kaiser, The accidental release of dense flammable and toxic gases from pressurized containment — transition from pressure driven to gravity driven phase, Paper presented at the 11th NATO/CCMS ITM on Air Pollution Modeling and its Applications, Amsterdam, Nov. 1981.
- 7 G.D. Kaiser, 'The accidental release of anhydrous ammonia to the atmosphere — Evidence for the occurrence of denser-than-air mixtures, *Loss Prevention Bull.*, 38 (1981) 1–22.
- 8 G. McMullen, A review of the 11th May ammonia truck accident, City of Houston Health Dep. Report., 1976.
- 9 Highway accident report; Transport Company of Texas, tractor-semitrailer (tank) collision with bridge column and sudden dispersal of anhydrous ammonia cargo, I-610 at Southwest Freeway, Houston, TX, May 11, 1976, US National Transportation Safety Board Report NTSB-HAR-77-1.

- 10 H. Lonsdale, Ammonia tank failure — South Africa, *Ammonia Plant Safety*, 17 (1975) 126—131.
- 11 Railroad accident report; Chicago, Burlington and Quincy Railroad Company train 64 and train 824 derailment and collision with tank car explosion, Crete, NB, Feb. 18, 1969, U.S. National Transportation Safety Board Report Number NTSB-RAR-71-2.
- 12 Railroad accident report; Louisville and Nashville Railroad freight train derailment and puncture of anhydrous ammonia tank cars at Pensacola, FL, Nov. 9, 1977, U.S. National Transportation Safety Board Report Number NTSB-RAR-78-4.
- 13 Pipeline accident report; Mid America Pipeline System anhydrous ammonia leak, Conway, KS, Dec. 6, 1973, U.S. National Transportation Safety Board Report Number NTSB-PAR-74-6, 1974.
- 14 J.G. MacArthur, Ammonia storage tank repair, *Ammonia Plant Safety*, 14 (1972) 1—5.
- 15 L.S. Fryer and G.D. Kaiser, 'DENZ-A computer program for the calculation of the dispersion of dense toxic or explosive gases in the atmosphere, UKAEA Report SRD R152, 1979.
- 16 A. Resplandy, Etude experimentale des proprietes de l'ammoniac, *Chim. Ind.—Gen Chim.*, 102 (1969) 691—702.
- 17 J.D. Reed, Containment of leaks from vessels containing liquefied gases with particular reference to ammonia, *Loss Prevention Symp.*, The Netherlands, May 1974.
- 18 B. Maurer, K. Hess, H. Giesbrecht and W. Leuckel, Modeling of vapour cloud dispersion and deflagration after bursting of tanks filled with liquefied gas, 2nd International Symp. on Loss Prevention and Safety Promotion in the Process Industries, Preprints pp. 305 et seq., DECHEMA (Deutsche Gesellschaft für Chemisches Apparateweser ev), Frankfurt, 1977.
- 19 K.A. Dietz (Ed.), STEP Project Quarterly Report, Oct.—Dec. 1966, IDO 17214, 1967.
- 20 J. McQuaid, HSE, Sheffield, Personal Communication.
- 21 P.K. Raj, J. Hagopian and A.S. Kalelkar, Prediction of hazards of spills of anhydrous ammonia onto water, NTIS AD 779400, 1974.
- 22 M.F. Flessner, U.S. Coastguard, Personal Communication.
- 23 G.A. Briggs, Lift-off of a buoyant gas initially on the ground, Air Resources, Atmospheric Turbulence and Diffusion Lab. Report, ATDL Contribution File No. 87 (Draft), 1973.
- 24 J. McQuaid, Examination of entrained air-flow rate data for large-scale water spray installations, Health and Safety Labs., Technical Paper 1, 1978.
- 25 O. Zeman, The dynamics and modeling of heavier-than-air, cold gas releases, University of Colorado Report UCRL-15224, 1980.
- 26 J.A. Havens, A preliminary computational analysis of proposed anhydrous ammonia release experiments, University of Arkansas Preprint (Performed for U.S. Coastguard, April 1980).
- 27 J.C.R. Hunt, Dispersion from non-buoyant sources near buildings, Review Paper for the United Kingdom Atmospheric Dispersion Modeling Working Group, Sept. 1978.
- 28 D.J. Hall, C.F. Barrett and A.C. Simonds, Wind tunnel model experiments on a buoyant emission from a building, Warren Spring Laboratory Report LR 355 (AP), Funded by the UKAEA Safety and Reliability Directorate, 1980.
- 29 Handbook of Chemistry and Physics, 53rd edn., Chemical Rubber Company, Cleveland, OH, 1972.
- 30 Hazardous Chemicals Data Book, Noyes Data Corporation, Park Ridge, NJ, 1980.
- 31 United States Coast Guard, CHRIS—Hazardous Chemical Data, 1978.
- 32 Chemical Industries Association, Code of practice for the large scale storage of fully refrigerated ammonia in the U.K., 1974.
- 33 Committee on Medical and Biological Effects of environmental pollutants (Subcommittee on ammonia), National Research Council, University Park Press, Baltimore, MD, 1979.

- 34 United States Dept. of Transportation, Hazardous Materials Incident Reporting System, Report on accident at Glen Ellyn (N 606004), 1976.
- 35 P.J. Baldock, Accidental releases of ammonia: an analysis of reported incidents, *Loss Prevention*, 13 (1980) 35–42.
- 36 Advisory Committee on Major Hazards, 2nd report, HMSO, London, 1979.
- 37 F.P. Lees, *Loss prevention in the process industries*, Butterworths, London, 1980.
- 38 D.C. Wilson, Flixborough versus Seveso — comparing the hazards, in: *Chemical Process Hazards VII*, Ind. Chem. Eng. Symp. series No. 58, 1980, pp. 193–208.
- 39 P.A. Carson and C.J. Mumford, An analysis of incidents involving major hazards in the chemical industry, *J. Haz. Mat.*, 3 (1979) 149–165.
- 40 V.C. Marshall, How lethal are explosions and toxic escapes. *The Chemical Engineer*, Aug. 1977, pp. 573–577.
- 41 L. de Temmerman, Les degats aigus et subaigus occasionnes aux plants par une décharge accidentelle d'ammoniac, *Revue de l'Agriculture*, 33 (1980) 763–776.
- 42 D.H. Slater, Vapour clouds, *Chemistry and Industry*, 6 May 1978, pp. 295–302.
- 43 R.N. Meroney, Lift-off of buoyant gas initially on the ground, *J. Industrial Aerodynamics*, 5 (1979) 1–11.