Methods for Assessing and Reducing Injury from Chemical Accidents
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11 *Dispersal of Chemicals*

James McQuaid

11.1 INTRODUCTION

The focusing of attention in recent years on the dispersion of gases released in chemical accidents has been brought about by the realization that the dispersion behaviour can be markedly different to that observed with atmospheric pollutants. The dispersion of pollutants has been studied for many years and much is known on the dispersion characteristics, derived from theoretical modelling, experimentation and observation. In contrast, until comparatively recently the phenomena involved in dispersal of gases released in large-scale accidents have been much less well understood. In addition to the pressure resulting from concern at the potential risk posed by the increasing scale of industrial and transport operations involving hazardous chemicals, there has also been the stimulus provided by the considerable scientific interest of the different phenomena. There has also, unfortunately, been the experience of actual accidents, as evidenced in the review by Vilain (this volume, Chapter 17).

Chemical accidents give rise to a new class of problems in dispersion prediction for the following reasons:

1. The material is, in almost all cases, stored as a liquid, so that the volume of gas evolved is very large.
2. The modes of release can vary widely from a ruptured pipe to a complete tank failure, whereas pollution problems almost invariably relate to covenanted chimney emissions. The geometry of the source can take many forms and the initial momentum may be significant. The site of the accident may not be a fixed location, as in transportation and pipeline accidents.
3. The process of formation of the gaseous cloud involves the phase transformation from liquid to gas. This can occur in a number of ways, from a flashing jet entraining air to the evaporation of a pool by heat transfer from the substrate.
4. In some cases, a chemical transformation also takes place as a result of reaction with water vapour in the ambient atmosphere, e.g. nitrogen tetroxide (N_2O_4), hydrogen flouride (HF).

5. The physical properties of the materials usually result in the formation of a denser-than-air (i.e. negatively buoyant) cloud, compared to the neutrally or positively buoyant gases in pollution problems. The negative buoyancy can have a marked effect on the dispersion characteristics.
6. The release can occur over a short time-scale, compared to the steady-state releases characteristic of most pollution problems. This gives rise to the complication of predicting dispersion for time-varying releases and to uncertainty in individual predictions resulting from variability about the ensemble mean behaviour.
7. The dispersing gas, where it is denser than air, forms a low-level cloud that is sensitive to the effects of man-made and natural obstructions and of topography.

These multi-faceted issues mean that an all-embracing review of assessment methods is beyond the scope of a single chapter. Some are not in the realm of the dispersion estimation itself but they cannot realistically be excluded from the consideration of dispersion. A discussion of the current state of knowledge on these latter issues is therefore included so that the dispersion problem is seen in its true perspective.

11.2 CHEMICAL ACCIDENTS

It is useful and informative to review the circumstances surrounding some recorded accidents in order to illustrate the variety of situations that confront the assessor. The review is neither comprehensive nor detailed, only the features relevant to the later discussion being highlighted.

11.2.1 Blair, Nebraska, USA

This accident occurred in 1970 and is described by MacArthur (1972). A very large tank of liquefied ammonia was overfilled. Over a period of two hours, a total of 160 tonnes of ammonia was released. The accident occurred at a remote location and no human fatalities resulted. The ammonia was maintained as a liquid at atmospheric pressure by refrigeration. Gaseous ammonia, even at the storage temperature of −33 °C corresponding to a vapour pressure of 1 atmosphere, is less dense than air despite its molecular weight of 17. However, the overflow from the tank was piped to ground level, at which point the hydrostatic pressure was 2 to 3 atmospheres. This pressurization resulted in a flashing jet of liquid. The jet entrained air and the cooling of the air resulted in an ammonia–air mixture with a density greater than that of the ambient air. The gas mixture spread over a large area, there being very little wind. The top surface of the cloud (made visible by condensed water vapour) was very stable, exhibiting a sharp interface that was quite noticeable in photographs. The

formation of denser-than-air clouds from ammonia releases is well documented and the conditions under which they occur have been described by Griffiths and Kaiser (1982).

11.2.2 Houston, Texas, USA

In this accident, which happened in 1976, a complete failure of a road tanker containing 19 tonnes of ammonia resulted after the tanker had fallen from an elevated roadway. There was a rapid formation of a large cloud which slumped to ground level and spread over the surrounding area. Six people were killed. The aftermath of the accident showed scorching of vegetation which marked the spread of the cloud. The edges of the scorched area were very distinct, resulting from the sharp interface at the cloud edge. A somewhat similar accident occurred at Potchefstroom, South Africa, in 1973 when a pressurized tank containing 38 tonnes of liquefied ammonia failed suddenly. The contents of the tank were released virtually instanteously and 18 people were killed as a result of exposure to the ammonia cloud.

11.2.3 Mississauga, Canada

In this case, a rail tankcar containing chlorine failed as a result of engulfment in a fire following a derailment. There were no injuries attributable to the chlorine. Although the breach in the tankcar was substantial (about 1 m diameter), it was found afterwards that not all the chlorine had been released. The quantity that is released when a rupture occurs is an important factor in the assessment of the consequences of an accident and will be further discussed later in the chapter.

11.2.4 Bhopal, India

The circumstances of this accident are so well known that they will not be repeated here. As far as the present context is concerned, the important features were that the cloud was denser than air and was emitted from a high-level vent as a gas (methyl isocyanate). The gas would therefore have bent over and fallen to the ground in the manner illustrated in Figure 11.1 (taken during some unpublished experiments in Buxton, England). The resulting low-level cloud in the accident spread over a large area and was only slowly dispersed by the wind. Its dispersion would also have been influenced by the presence of the many buildings in its path.

These disparate examples show the wide range of conditions that can occur in accidents.

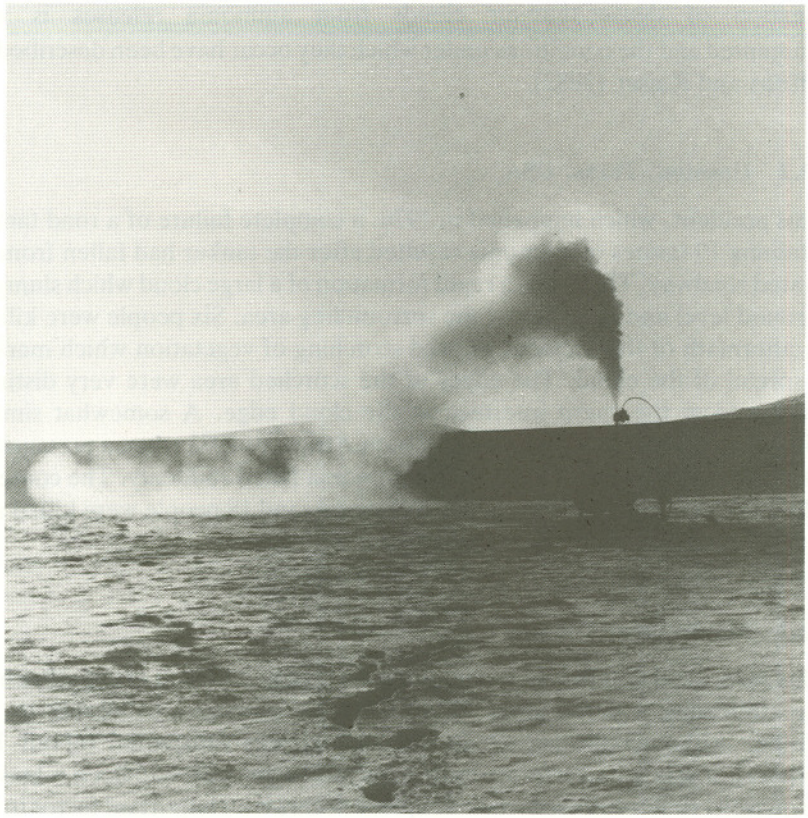

Figure 11.1 The vertical emission and return to ground level of a denser-than-air jet

11.3 THE ASSESSMENT OF INJURY FROM CHEMICAL ACCIDENTS

The estimation of dispersion is used in the assessment of injury from chemical accidents both as part of planned measures for accidents that might occur and of the follow-up investigation and institution of remedial measures for accidents that have occurred.

It will be clear from the foregoing that the procedure for estimating the consequences of potential accidents has the following components:

1. The mathematical description of the processes by which the cloud is formed. This is necessary to provide the input parameters for the dispersion calculation, for any particular postulated event.
2. The mathematical description of the dispersion process, providing the concentration of gas as a function of space and time.
3. The description in quantitative terms of the likely injury to populations and

damage to the environment as a result of exposure to the concentration – time history derived from (2).

The first of these requires that the postulated event should be specified. This is a subject in its own right and involves a systematic analysis of the ways in which loss of containment can occur as a result of inherent defects in equipment or of excursions of plant operating conditions beyond the design capability. Such an analysis also necessarily includes consideration of the associated probability per unit time of the failure mechanisms. Methods by which this exercise can be carried out are considered by Vilain (see this volume, Chapter 17). Attention will be confined in this chapter to the physical results of the failure as determinants of the dispersion process, together with the second of the above components. The third component is considered in full in other chapters in this volume. The amelioration of injury as a result of mitigating factors such as being indoors, escape from the cloud, etc., is considered in some detail by Davies and Purdy (1986).

In the estimation of dispersion following an actual accident, the release mechanism may be self-evident, or dispersion estimates may be coupled with observations of damage in order to discriminate between candidate explanations of the accident sequence. The dispersion estimate provides necessary information on exposure levels with potential long-term effects so that remedial measures as described elsewhere in this volume, can be properly planned.

For convenience, references to the dispersing gas in the foregoing have been to a cloud. It is conventional to refer to a cloud when considering an isolated volume from a release of short duration. A release that is sustained for a long time is referred to as a plume. This convention will be followed in the remainder of the chapter. The time differentiation between a cloud and a plume is somewhat arbitrary and will be considered in more detail later.

11.4 THE FORMATION PHASE

The processes governing the formation of a cloud or plume determine the 'source term' for the dispersion phase. The essential requirements are to be able to specify the release rate or total quantity released, the physical properties and the initial geometry of the cloud or plume. The parameter values are required at the time when source-specific effects have subsided, e.g. the momentum of release. The types of source for which the conditions need to be defined can be classified according to (*a*) the storage conditions; (*b*) the geometry, e.g. pipe breaks, catastrophic vessel failures, etc.; and (*c*) the surroundings into which the material is released, e.g. bunds, unconfined ground or water.

The behaviour during release depends strongly on whether the liquid is

pressurized or refrigerated, or more precisely, on the degrees of superheat possessed by the liquid. The superheat is the elevation of the storage temperature above the boiling point at atmospheric pressure (often referred to as the 'normal boiling point'). A liquid with zero superheat is said to be 'fully' refrigerated.

11.4.1 Releases from Pressurized Storage

A gas maintained as a liquid by storage under pressure is usually also at the ambient atmospheric temperature. Examples of gases commonly stored or transported in this condition include chlorine, ammonia and liquefied petroleum gases such as propane and butane. Engineering limitations on the size of pressure vessels mean that individual storages of this type are limited to around 150 and 200 tonnes capacity. The storage temperature can also be below ambient atmospheric temperature but still above the normal boiling point of the liquid. The storage condition is maintained by refrigeration, referred to as 'partial' refrigeration in this case. Because of the lower pressures, sizes can be larger, ranging up to about 2000 tonnes. Ammonia is sometimes stored in this way in spherical vessels. The temperature of the liquid can sometimes be above ambient temperature, generally as a result of the material undergoing a process rather than being in store. Sometimes also the pressure may be maintained above the saturation vapour pressure of the liquid at ambient temperature by pressurizing with a second gas, a condition known as padding.

Irrespective of which of these methods is used, a loss of containment will cause the pressurized liquefied gas to be ejected violently. There is a variety of possible release conditions depending on whether the breach in the vessel is above or below the liquid level, the size of the breach in relation to the cross-sectional area of the vessel, the actual storage conditions and the physical properties of the material. A detailed discussion of the various circumstances, with particular reference to ammonia as an example, is given by Griffiths and Kaiser (1982). A fundamental study at laboratory scale of the effects of superheat on the fraction of liquid that is discharged has been carried out by Fletcher (1982). He provides specific guidance and he corroborated his conclusions by comparing estimates of liquid fraction discharged with observations in several large-scale accidents. A general feature, as observed in accidents and experiments, is the evolution of a rapidly expanding two-phase cloud. The phase composition (i.e. vapour/liquid mass ratio) of this cloud depends on the initial stored energy in the liquid which in turn depends on the superheat, results for which have also been given by Fletcher (1984). As the superheat increases, so vapour–liquid disengagement in the vapour space of the vessel decreases and an increasing proportion of the liquid is entrained by the erupting vapour and is carried out of the vessel. Some of the liquid is in the form

of large drops which rain out of the cloud and so do not contribute to the volume of vapour that goes to form the cloud. The expanding cloud reaches a maximum size whose final composition depends on the rate at which it entrains air.

As to quantitative guidance on these matters, the two factors that are needed are (*a*) the volume of vapour that becomes airborne and (*b*) the volume of air that is entrained by the vapour during the initial expansion. These together provide the required source quantity for the dispersion calculation. A common assumption is that the allowance for the liquid fraction that contributes to the vapour cloud should be made by doubling the theoretical vapour flash fraction. (This fraction is derived from a simple heat balance, equating the loss of sensible heat of the remaining liquid to the latent heat of vaporization supplied to the vapour.) This assumption has no theoretical foundation and was at one time widely adopted as a rule of thumb in the absence of anything better. It was questioned in the Second Report on the Canvey Island Investigation (Health and Safety Executive, 1981). This report studied the potential risks from a collection of chemical installations around Canvey Island in the United Kingdom. The investigation provides detailed guidance on the technical issues involved in the assessment of injury from chemical accidents and is still a recommended first reading for those new to the subject. On the basis of calculations performed in that report, together with a reappraisal by Grint (1984) and taking account of the work of Fletcher (1984), it would seem more realistic to assume that the whole of the vessel contents becomes vaporized, subject to the reservation that where the superheat and/or the area ratio is low, the quantity can be reduced in accordance with Fletcher's results. The subject is by no means closed, however, and further work to refine this guidance is in progress.

On the question of the amount of air entrained, another rule of thumb is that the volume equals 60 times the vapour flash fraction, independent of material properties and physical conditions. This is based on evidence from accidental releases of pressurized ammonia examined by Kaiser and Walker (1978), although it must be said that the evidential support is slight indeed. Analyses of the amount of air entrained up to the time when the pressure-driven expansion has subsided have been carried out by Jagger and Kaiser (1981) and Griffiths and Kaiser (1982). However, comparison with experimental evidence was not possible and that indeed is still the case. There is a great need for work in this area and the subject is being actively pursued in a number of institutions. The topic has been accorded the highest priority for research action in the immediate future by the Commission of the European Communities. In the meantime, the only recommendation that can be made (and which reflects good practice) is to test the sensitivity of the conclusions to the assumption about entrainment. For toxic gases, with dilutions of a factor of 10^5 or more required to make them safe, the uncertainty in the initial dilution is often not a significant factor in the overall uncertainty in the distance to achieve a given concentration.

Non-catastrophic failures, such as pipebreaks or small penetrations of vessels, result in a jet which will exhibit a steady-state behaviour. Two items of information are required – the rate of release and the growth rate/velocity decay of the jet – in order to specify the initial conditions for the dispersion calculation. If the release is single-phase vapour from the vapour space, the release rate is determined by standard well-known methods (see for example Artingstall, 1972). The problematical area arises with two phase vapour/liquid releases from below the liquid level. Specific guidance on release rates is included in Health and Safety Executive (1981). Further developments since then include the comprehensive investigation by the Design Institute for Emergency Relief Systems (Fisher, 1985) and work by Fletcher (1984) and Fletcher and Johnson (1984).

In relation to the growth rate and velocity decay of the jet, for a single-phase gas reference should be made to recent work by Brennan *et al.* (1984) and Ewan and Moodie (1986) which particularly addresses the case of underexpanded jets not treated in standard works. The interaction of the jet and the wind, and the transition from a momentum-dominated jet to a plume dominated by atmospheric-turbulence-induced entrainment and buoyancy are included in the model described by Ooms *et al.* (1974). For two-phase jets, the position is much less satisfactory and no clear guidance is available; work is in progress on the problem. The review by Appleton (1984) is a useful source of information.

The effects of the surroundings into which the material is released have to be decided by judgement. For a catastrophic failure, the presence of a bund or obstruction in the vicinity will have little effect on the cloud expansion – the size of the final cloud will be so large in relation to the size of the storage vessel that this is quite a safe assumption. For a non-catastrophic failure, it will obviously be of crucial importance whether the jet impacts an obstruction or not. There is no realistic way to allow for this and the worst case assumption, i.e. no initial dilution, must be used.

11.4.2 Releases from Fully-Refrigerated Storage

The estimation of the quantity released or the release rate is rather simpler than for pressurized releases. The complication of two-phase flow is absent, except where there is a significant hydrostatic pressure as in the Blair accident described earlier.

The surroundings have an important role in determining the rate of evolution of vapour from the spilled liquid. The liquid will either be contained in a bunded area or will form a spreading pool on the ground (or on the sea as appropriate). Where the liquid temperature is substantially below the ambient temperature (as for example in the case of LNG with a normal boiling point of −162 °C), the evaporation rate per unit area depends on the physical properties of the liquid and the thermal properties of the surfaces contacted by the

liquid. Analytical models are available (for example Shaw and Briscoe, 1978), while Prince (1985) has compared predictions with the results of experiments. A complication is that the evaporation rate per unit area decreases with time as the ground cools. A calculation based on the initial temperature will usually be satisfactory. It will be conservative (i.e. will overestimate the source term for later times) and will be compatible with the requirements of the simpler, more widely used, dispersion models.

For liquids with a boiling point not too far below ambient temperature (e.g. chlorine, ammonia, propane, butane) heat transfer from the wind becomes important and may dominate heat transfer from the contacted surfaces. Good progress has been made in resolving the problem of estimating the evaporation rate. The recent paper by Brighton (1985a) is an important development.

The area of the evaporating surface is often fixed by the presence of a bund so that no difficulty in specification arises. Where the spread of the liquid pool is unconfined, estimates of the rate of spread and of the ultimate steady-state diameter attained (in cases where the release is itself sustained) must be made. The rate of spread has been studied for a variety of conditions by Webber and Brighton (1984). These developments are currently being incorporated into an updating of the widely used computer code SPILL (Prince, 1982).

11.4.3 The Specification of the Source Team

The specification of the initial conditions of the cloud or plume for the dispersion calculation obviously must take account of any restrictions imposed by the dispersion model. In general, it is necessary to specify the size, shape and physical composition of the initial cloud, or the size and shape of the source and the physical composition of the emission for a plume.

The box model of dispersion, in wide use and to be described later, makes quite restrictive assumptions about the initial shape. It assumes, for a cloud, that the shape is that of an upright circular cylinder. The volume, as estimated by the procedures outlined in Sections 11.4.1 and 11.4.2, must be combined with a further assumption about the aspect ratio (ratio of height to diameter) to obtain the geometry of the cylinder. The effect of initial aspect ratio on the early stages of dispersion of the cloud is still somewhat uncertain.

For a plume, it will usually be possible to specify the lateral dimension at the source without difficulty. It can be done directly from the results of the analysis of the formation phase, e.g. the diameter of an evaporating pool, or, with more sophistication, by taking account of gravity spreading of the vapour beyond the edge of the pool. A useful correlation for this effect has been given by Britter (1980). Once the lateral dimension is specified, the known volume flow rate together with an assumption for the initial advection velocity of the plume provides the initial plume depth. The advection velocity is related in some way to the velocity profile of the wind, sometimes as the velocity at a fixed fraction

of the initial depth (in which case an iterative calculation is needed). The actual specification is a matter of choice by the modeller. For the dispersion of highly toxic gases, any assumption (within reason) for the initial plume depth is likely to be satisfactory at the dispersion ranges of interest.

11.5 GENERAL CHARACTERISTICS OF DISPERSION FOLLOWING CHEMICAL ACCIDENTS

The characteristic that most frequently influences dispersion following chemical accidents is the excess density of the released gas. Thus dense gas dispersion (as it is known) will be the main concern of this chapter. However, passive dispersion (where the dispersing gas does not affect the structure of the flow) also has to be considered. A release that exhibits dense gas effects at the source will ultimately progress to passive behaviour. There will also be accidents where the dispersion is passive from the source. This occurs if the size of the release is small enough or the windspeed is high enough, even though the released gas is denser than air. Quantitative criteria for determining whether passive dispersion applies from the source will be given later.

Observations following accidents and in controlled experiments show that the effects of the excess density are most obviously manifested in a greatly increased spread of the cloud or plume in the lateral (cross-wind) direction and a much reduced vertical extent. The dense gas may also move against the wind. It will preferentially follow the ground slope and may move down a slope in opposition to the wind. It may flow around obstacles rather than around and over them and, if the obstacle is two dimensional, e.g. a wall, the flow may be blocked.

Some of these features are well illustrated in photographs from large-scale field experiments, e.g. Koopman *et al.* (1982); Puttock *et al.* (1982); McQuaid and Roebuck (1985). The latter reference reports a study of the dispersion of clouds of dense gas carried out at Thorney Island, England. The cloud in each of the experiments was formed in a container which could be rapidly removed. The container was 14 m diameter and 13 m high and the gas was stored in it at ambient temperature and pressure. Following the removal of the container, the cloud rapidly slumped and spread radially, forming a pronounced gravity front. Figures 11.2(a) to 11.2(c) show several stages in the early motion of the cloud viewed from the side and Figures 11.3(a) to 11.3(c) show views from an overhead camera. The experimental design was intended to be consistent with the sequence of events following a release from pressurized storage, as described earlier. The initially stationary cloud represented the end result of the formation phase. The design was also compatible with the geometry assumed in box models of dispersion.

Plume experiments were also carried out in the Thorney Island series. The plume was several hundred metres wide but no more than about 2 m deep, a

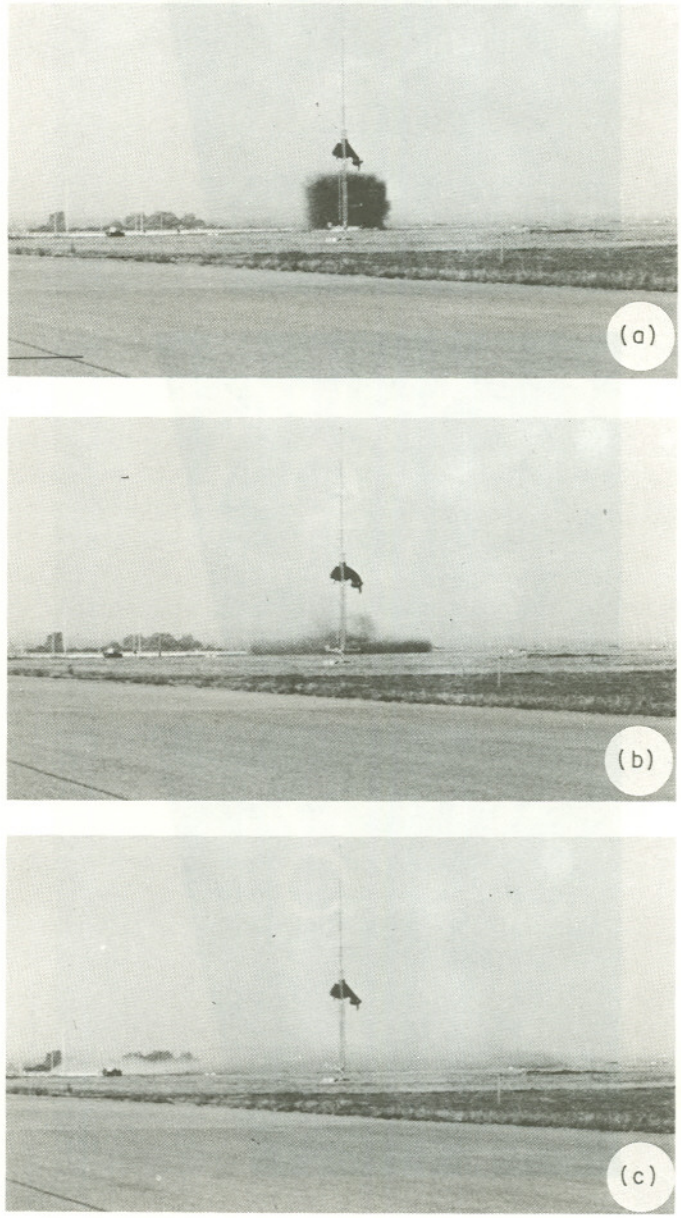

Figure 11.2 The gravitational collapse and spreading of a dense gas cloud. (a) Release of the cloud. (b) After a further 3 seconds. (c) After a further 24 seconds

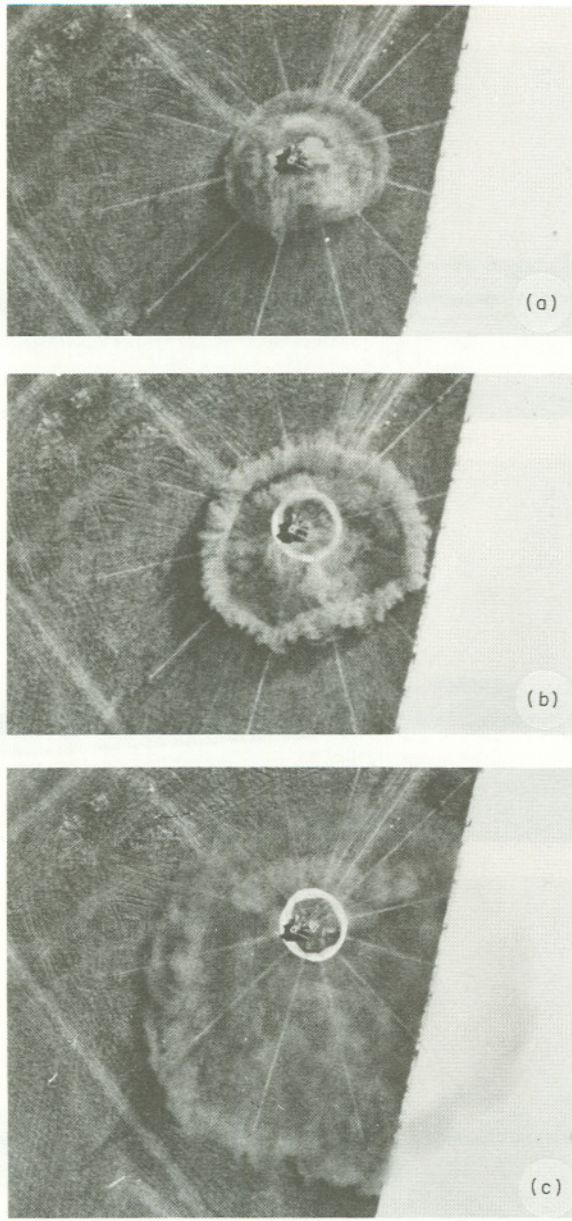

Figure 11.3 The spreading of a dense gas cloud as seen from above. The white strip is the runway of the airfield on which the experiment was performed. (a) About 3 seconds after release. (b) After a further 2.5 seconds. (c) After a further 10 seconds

geometry in marked contrast to that characteristic of passive dispersion. It was also observed that the interface between the dense gas and the ambient atmosphere showed little of the highly turbulent engulfing motions found with passive plumes.

The excess density markedly affects the entrainment of ambient air by the cloud or plume and thus the rate of increase of depth. However, this is to an extent counterbalanced by the increased lateral spread so that the downwind distance to a given ground-level concentration may not be much different from that for a passive cloud or plume of the same (volumetric) source strength.

Dense clouds or plumes also have a lower advection velocity (expressed as a fraction of a representative windspeed) and exhibit much less meander than is observed with passive releases. Releases of dense gas may modify the mean and turbulent structures of the atmosphere at heights above that occupied by the dense gas. This has been observed in laboratory experiments (McQuaid, 1976) and in field experiments (Koopman *et al.*, 1982; Mercer and Davies, 1987). The phenomenon has been discussed by McQuaid (1984a) and Hunt *et al.* (1984).

The proliferation of complex physical effects outlined above and the relative youth of the subject mean that presently available models can only be approximate representations of the physics of the problem (aside from the fact that any model of a turbulent flow phenomenon is at present an approximation). A considerable effort is in progress worldwide on the investigation of the various issues and developments in modelling are taking place quite rapidly. The complexity of the problem inevitably causes difficulties in deciding when a model has been properly validated against experiment – a factor of prime importance to assessors who wish to use a model.

In circumstances such as those outlined, physical modelling (in wind or water tunnels) has an important part to play. Good progress has been made in establishing scaling procedures and in achieving reproducibility of large-scale results. However, the topic is outside the scope of this chapter and the reader is referred to papers by Hall *et al.* (1982); Hall and Waters (1985); Meroney and Neff (1980); Meroney (1982); Van Heugten and Duijm (1985); Davies and Inman (1987); Spicer and Havens (1985).

A review of requirements for physical modelling is given by Meroney (1987).

11.6 DISPERSION OF DENSE GASES

11.6.1 Introduction

The dispersion of a dense gas cloud or plume proceeds through several phases, dependent on the dominant physical mechanism involved. For an extended discussion, the reader is referred to Hunt *et al.* (1984). Only a summary will be presented here as an introduction to modelling methods.

Firstly, there is a gravity-spreading phase in which the mixing is governed by entrainment across the edge and top of the cloud as a result of the gravity-induced motion. The former component is the more important. This phase includes the initial interaction between the cloud and the wind and the distortion of the cloud thereby produced. There follows a phase in which mixing by atmospheric turbulence is influenced by gravitational forces and the gravitational forces continue to produce enhanced lateral spreading of the cloud. Finally, the gravity influence subsides as the density difference between the cloud and the ambient air becomes small and mixing by atmospheric turbulence becomes dominant, i.e. passive dispersion prevails. There are several important and physically distinct problems associated with these phases which must be taken into account in modelling.

The first concerns the initial gravitational slumping of the cloud. The interaction of the wind field with an isolated cloud of dense gas and the resultant distortion of the cloud have been considered by Rottman *et al.* (1985). They were particularly concerned with the formation of the ring vortex very evident in Figure 11.3. They gave the time-scale for its formation and also estimated the time when the box model becomes an appropriate description of the cloud. They concluded that the structure of the cloud, and hence the initial dilution, is strongly dependent on the aspect ratio of the initial cloud. Webber and Wheatley (1987) analysed the effect of the turbulence generated from the initial potential energy of the cloud on the subsequent dilution and concluded that the effect is small. Although direct experimental evidence is lacking, they suggest that their conclusion is consistent with indirect evidence from the later stages of cloud development.

The description of the gravity-spreading phase draws on many studies of the motion of gravity fronts by, for example, Rottman and Simpson (1983) and Britter and Simpson (1978). The mixing across the density-stratified interface between the top surface of the cloud and the atmosphere has been, and still is, the subject of intensive study, both in the current context and in density-stratified flows that occur widely in nature (see, for example, Turner, 1973; Thomas and Simpson, 1985).

The processes involved in the passive dispersion phase are described in standard works, e.g. Pasquill and Smith (1983). The progression from gravity-influenced to passive dispersion can be modelled as a continuous process or by making the somewhat artificial assumption of an abrupt transition from one regime to the other. The transition is taken to occur when a criterion (for example, equality of the rate of lateral spreading with that for passive dispersion) is satisfied.

There are two questions that first have to be decided: when are density effects likely to be important in a given problem and which of instantaneous (cloud) or steady-state (plume) descriptions is appropriate.

11.6.2 Passive Versus Dense Gas Dispersion

Quantitative criteria have been given by Puttock *et al.* (1982) and Britter (1980) and have been reviewed by Britter and McQuaid (1987) in the light of the available experimental evidence. They recommend that passive dispersion results may be used as follows:

1. For a steady-state release of q_o m^3/s the criterion is

$$\frac{g'_o q_o}{U^3_{ref}} / D^{1/3} \leqslant 0.15$$

where U_{ref} is the windspeed at a reference height of 10 m, D is the characteristic horizontal dimension of the source and g'_o is the reduced gravitational acceleration at the source $= g(\rho_o - \rho_a)/\rho_a$ where ρ_o is the initial density of the gas, ρ_a is the density of the ambient air and g is gravitational acceleration.

The characteristic dimension of the source depends on the release configuration. It may, for example, be the diameter of an evaporating liquid pool or the plume width from a jet after source momentum effects have become unimportant.

2. For an instantaneous release of Q_o m^3, the criterion is

$$\left(\frac{g'_o Q_o}{U^2_{ref}}\right)^{1/2} / Q_o^{1/3} \leqslant 0.2$$

It should be noted that any allowance for initial dilution only affects the characteristic source dimension, $Q_o^{1/3}$, in the denominator. The product $g'oQ_o$ is unchanged; it is the total negative buoyancy of the cloud and is unaffected by dilution (provided there is no heat transfer to the cloud). The actual dilution factor to be applied has been discussed earlier. The evaluation of the criterion is not sensitive to the value of the dilution factor used because of the one-third power.

11.6.3 The Release Type

The simpler models of dispersion are formulated for either instantaneous or continuous releases. These are idealizations of what happens in practice and a question often arises as to which model formulation should be used in the assessment of any particular postulated accident. Various criteria that might be used to classify field experiments as instantaneous or continuous have been reviewed by Puttock *et al.* (1982) and that work is relevant also to deciding the choice of model in hazard assessment. The problem has also been discussed by Cox and Carpenter (1980) and Bradley *et al.* (1982). Britter and McQuaid (1987) have examined the rather sparse data and suggested that a release of duration T_o will be perceived as continuous at a distance x from the source if

$$\frac{U_{\text{ref}}\, T_{\text{o}}}{x} \geqslant 2.5$$

For a release to be deemed as instantaneous, they suggested the criterion

$$\frac{U_{\text{ref}}\, T_{\text{o}}}{x} \leqslant 0.6$$

These criteria do not classify releases uniquely as one or the other type – that depends also on the position of the observer. They are in accord with the fact that an observer far from the source will see a release as instantaneous that would be observed as continuous near to the source. The use of an instantaneous formulation to satisfy the needs of the far-field observer will give predicted concentrations in the near field that are larger than would be observed, so that the approach is conservative. The use of a continuous formulation, again dictated by the far-field observer, will be satisfactory to the near-field observer.

When the criteria given above indicate that the release is neither instantaneous nor continuous, it is generally satisfactory to perform upper limit calculations. As pointed out by Puttock *et al.* (1982), calculations using the two extreme possibilities provide conservative estimates of the concentration at a given distance. That is to say, an intermediate release will give concentrations lower than the same quantity released faster or concentrations no greater than those from a release at the same rate for a longer time.

11.6.4 Types of Dense Gas Dispersion Model

Dense gas dispersion models can conveniently be classified as box, intermediate (or slab) and 3-D. The distinguishing feature is the way in which the models represent the distribution of properties within the cloud or plume. Box models assume that all properties are distributed uniformly over the volume of the cloud or a transverse slice of the plume. 3-D models retain spatial distribution of properties in all three coordinate directions. Intermediate models apply some kind of spatial averaging in the vertical direction and thus fall between the other two types in their complexity. Although many models have been published by different authors, they exhibit a considerable degree of commonality within each type. All the 3-D models so far published use the gradient transfer hypothesis for turbulence closure (although turbulent stress modelling to provide closure is under development by a number of workers). Webber (1983) reviewed the variety of box models and found that all the published box models fall into one or other of two basic classes. He derived analytic solutions for the two classes, subject to the restriction that buoyancy was conserved (i.e. that there was no heat transfer to the cloud). Within this framework, he was able to highlight the differences in scaling properties incorporated in the models in an explicit and illuminating way.

Box models, because of their relative simplicity, can readily be assessed for the physical correctness of their assumptions, especially in the framework proposed by Webber (1983). They can be readily compared with experimental results, in isolation from any numerical solution procedure that might be used to solve the model equations. The model is centred on an equation for the rate of increase of mass of the cloud as a result of entrainment of ambient air. This entrainment is hypothesized to be compounded of entrainment through the edge of the cloud and through its top surface. The two processes are modelled separately. They make a changing relative contribution to the growth of the cloud. Near the release position, edge entrainment is dominant and decreases in importance as the cloud spreads and moves away from the release position (in the presence of a wind). Numerical solution of the model equations is straightforward and, in some formulations, analytic solutions are possible. They are cheap to run and are now readily usable as an everyday working tool. However, they cannot be applied without further development (and some heroic assumptions) to problems involving complex terrain or time-varying releases.

It is clear from inspection of Figure 11.3 that the assumption of a uniform concentration distribution is a gross simplification. However, the volume averaging applied in box models is consistent with practice adopted for other turbulent flows. The assumption of a uniform distribution, coupled with an entrainment hypothesis, has found wide application to jets, wakes and plumes and provides useful practical results without having to resort to numerical solution of approximations to the 3-D conservation equations. McQuaid (1984b) has discussed the merits of the box model and concluded that at the present time there is no strong case for replacing it with more complex models, at least for straightforward applications. It fulfils the same role in dense gas dispersion prediction as the widely used Gaussian model for passive dispersion to be described.

3-D models use basic equations which are reasonable approximations and are in principle applicable to complex terrain and time-varying releases. The validity of the gradient transfer hypothesis that they use is questionable for dense gas dispersion. The solutions are obtained using numerical integration schemes which are not usually separately evaluated for their contribution to the overall errors in prediction. It is therefore difficult to make judgements on the accuracy of the models based on the comparison with experiment that have been published. They are expensive to develop and to run and thus are unsuited for use in routine assessment. A comprehensive evaluation of some of the available 3-D models has recently been completed by Havens *et al.* (1987).

Intermediate models retain many of the advantages of 3-D models while largely avoiding the possible numerical solution problems. Analytic solutions are possible in some cases. Their development and running costs fall between those of the other two types. They have been comparatively neglected up to the present but this situation shows signs of changing.

A particularly comprehensive review of the different types of model has been given by Wheatley and Webber (1984). It provides an objective and rigorous assessment of models and also describes how the box model could be improved to correct the deficiencies they identify.

It is beyond the scope of this chapter to develop the equations for 3-D and intermediate models and to describe the way in which the turbulence closure assumption is incorporated. It is instructive, however, to consider the structure of box models in a general way and this will be done in the following section.

11.6.5 The Box Model of Dense Gas Dispersion

In order to illustrate the features of box models, a particular model is selected. This is the generalized Picknett model, originally presented by Picknett (1981) and generalized by Wheatley *et al.* (1986). The model is quite typical of box models. It has been selected because comparisons are available of the model predictions with the data from Thorney Island experiments which have been used for illustration in this chapter. The presentation below draws directly on the paper by Wheatley *et al.* (1986) to which the reader is referred for more information.

The structure of the cloud as represented in the model is shown in Figure 11.4 The edge of the cloud spreads radially with a velocity given by the equation for the velocity of a gravity front, i.e.

$$U_f = \frac{dR}{dt} = (g'H)^{1/2} \tag{1}$$

where R is the cloud radius, H the cloud height, g' the reduced gravitational acceleration as defined earlier and K is a dimensionless constant with a value of about 1.07. Equation (1) can be rewritten as

$$U_f = \frac{kb^{1/2}}{R} \tag{2}$$

where b is proportional to the total negative buoyancy of the cloud. Isothermal conditions are considered so that b remains constant independent of dilution of the cloud.

The rate of growth of the cloud volume, V, is written as

$$\frac{dV}{dt} = 2\,\pi RH\,U_E + \pi\,R^2\,U_T \tag{3}$$

The first term on the right-hand side represents the rate of entrainment across the cloud edge and the second the rate of entrainment across the cloud top surface.

The edge entrainment velocity, U_E, is assumed to be proportional to the front velocity, i.e.

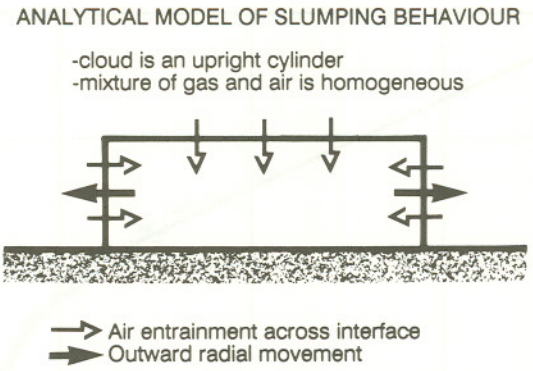

Figure 11.4 The geometry of the box model of dense gas dispersion

$$U_E = \alpha_E U_f \tag{4}$$

The top entrainment velocity, U_T, will be dependent on the density stratification at the top surface, as discussed earlier. It is written as

$$U_T = \alpha_T U / Ri^{\mu} \tag{5}$$

U is an appropriate velocity scale of the ambient atmospheric turbulence and is represented in different ways in different models. Ri is a Richardson number defined by

$$Ri = \frac{g'H}{U^2} \tag{6}$$

Both α_E and α_T are dimensionless constants less than unity and are called the edge and top entrainment coefficients respectively. The index μ in equation (5) is also a constant and is assigned different values by different modellers depending on their view on the mechanism of turbulence suppression by the density stratification, a topic discussed in detail by Thomas and Simpson (1985).

The above equations can be solved to give the cloud-averaged concentration, C, as

$$\frac{C_o}{C} = \frac{V}{V_o} = (1 - \gamma)\tau^{\alpha_E} + \gamma\,\tau^{\mu+2} \tag{7}$$

where V is the cloud volume and subscript o represents conditions at the source. τ is the time, non-dimensionalized with a time constant related to the total buoyancy and γ is a constant related to the other constants in the formulation (including the specified initial cloud properties). In practice, γ is

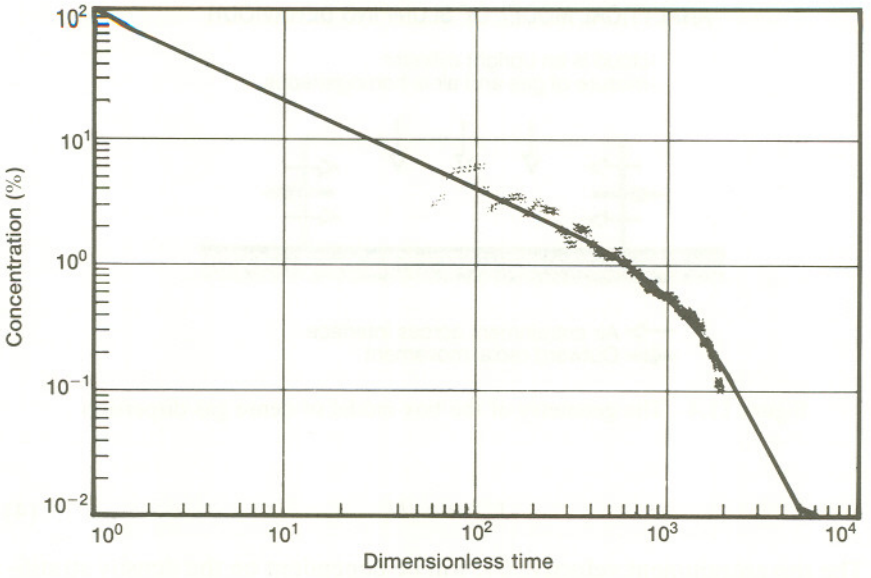

Figure 11.5 The fit of a generalized box model to large-seale field data (from Wheatley *et al.*, 1986). The data are from trial number 17 of the Thorney Island series

very much less than unity and so equation (6) shows that at small times the dilution is determined by the first term (i.e. by edge entrainment) and at large times by the second term (i.e. by top entrainment).

These general conclusions are well supported by the results of the Thorney Island experiments. Furthermore, Wheatley *et al.* (1986) were able to select values of the adjustable constants which gave good agreement with all the results of the experiments, which comprised sixteen trials at widely different windspeeds and atmospheric stabilities. An example of the fit to the concentration data is shown in Figure 11.5. It should be noted that the determination of the average cloud concentration from the experimental data is a separate (and quite elaborate) exercise and was carried out by Brighton (1985b).

11.6.6 The Effects of Obstructions on Dense Gas Dispersion

Most of the experiments on record have been performed on flat sites with uniform roughness. Similarly, most of the available models are restricted to those conditions. The situations in which chemical accidents occur are unlikely to conform to these restrictions. It is necessary to consider how obstructions, both natural and man-made, affect dispersion of dense gases. It is of course logical that the simplest situation of flat ground should be addressed as a first priority.

As resolution of the simple case is at hand, attention is now being directed to the added complication of an obstruction. It should be stated that the assumption of a uniform unobstructed field will, as a general rule, give a conservative answer for the concentration at any particular distance from the source. However, there are possible complications which this assumption does not cover. For example, the obstruction (or a ground slope) may substantially deflect the path of a cloud or plume from the mean wind direction. Another problem of interest is whether a dense gas will surmount a crosswind fence or will spread laterally along it.

There is much to be done before guidance on these issues can be given but progress is being made. A review of the physical effects on dense gas dispersion of various kinds of obstruction and topographical features was carried out by Britter (1982). The Thorney Island experiments included a study of the effects of various kinds of obstruction on the dispersion of dense clouds and an extensive body of data is now available. A summary of the results has been given by McQuaid (1986). Laboratory experiments have been reported by Kothari *et al.* (1981) and Davies and Inman (1987). Further work is in progress and rapid developments can be anticipated in the next few years.

For passive dispersion, guidance on the effects of obstructions is given in Jones (1983).

11.6.7 The Effects of Atmospheric Stability

When the atmospheric wind conditions are gusty or turbulent it is a matter of common observation that a pollutant plume spreads rapidly. Gustiness is related to the stability of the atmosphere. A neutrally stable atmosphere is one where a parcel of air which is displaced from one level to another always attains the density appropriate to its new position, a condition that prevails when the temperature falls by about 1 °C per 100 m, called the adiabetic lapse rate. An unstable atmosphere is one where the temperature decreases more rapidly than the adiabatic lapse rate. Thus a parcel of air which is displaced upwards will be subject to a buoyancy force which causes it to continue moving upwards and similarly if it is displaced downwards it continues to move downwards. Disturbances are therefore amplified and turbulent mixing is increased. The converse applies if the temperature decreases less rapidly than the adiabatic lapse rate, as occurs in a stable atmosphere, also known as an inversion.

In addition to the effect on turbulence, the atmospheric stability also affects the vertical profile of mean velocity. For a full description of these effects, reference may be made to Lumley and Panofsky (1964).

For passive releases, the stability has a large effect on the rate of dispersion. The downwind distance to a given concentration in stable conditions can be larger by two orders of magnitude than in unstable conditions. The effect on dense gas dispersion is rather less pronounced. This is because the density

variation within the gas cloud (which of course is stably stratified in the sense discussed above) is very much larger than the density variation in the atmosphere, even under the most stable conditions. The stability influences the turbulence level in the ambient atmosphere which in turn influences the entrainment through the top surface of the cloud. This is parameterized in the box model described in Section 11.6.5 by the turbulence velocity scale in equation (5). However, the experimental evidence available for delineating the effect is not very conclusive. The Thorney Island experiments covered a wide range of atmospheric stability but McQuaid and Roebuck (1985) found no immediately apparent effect of stability on the distribution of the maximum ground-level concentration. A more detailed analysis of the same data by Brighton and Prince (1987), in which the computed cloud-average concentration data were examined, suggested that significant differences (above the level of experimental variability) could be discerned, especially at the unstable end of the range covered by the experiments. Morgan *et al.* (1984), in analysing the results of experiments on liquefied natural gas at China Lake, USA, found that the distance to a given concentration increased with atmospheric stability. Britter and McQuaid (1987) tentatively suggest, from the results of the China Lake experiments, that the proportional influence of atmospheric stability on dense gas dispersion is about half that for a comparable passive release.

11.7 PASSIVE DISPERSION

Although dense gas dispersion is usually the dominant consideration in large-scale chemical accidents, as explained earlier any dense gas release eventually progresses to a stage where the normal atmospheric mixing processes become dominant and the dispersion enters the passive phase. A comprehensive account of this subject is given in Pasquill and Smith (1983) while Turner (1970) presents estimation methods in workbook format. Since the technology is well established, only a brief qualitative description of the main features will be presented and attention will be restricted to the Gaussian model. As with dense gas dispersion, there are available more complex models based on turbulence closure. Indeed, the dense gas dispersion models of this type usually start life as passive dispersion models. The Gaussian model has been in widespread use for over 20 years. Refinements continue to be made to it. The empirical content has been adapted to incorporate new information and allowances for such factors as ground roughness and building wakes have been introduced.

The starting point of the method is the solution of Fick's Law of Diffusion in three dimensions for a point source of material released instantaneously. 'Point' and 'instantaneous' sources are mathematical abstractions useful in obtaining solutions to the governing equations. Fortunately, the way in which practical sources deviate from these idealizations causes the derived estimates to err on the safe side. Thus a source of finite size is equivalent to a point source

at some point further upwind. Distances calculated for a point source will therefore be larger than for an actual source. Similarly the concentration resulting from a release that takes some short time to be completed will be lower at all points downwind than for an instanteous release of the same amount of material. From the solution for an instantaneous point source, extensions to continuous releases and to line and area sources are readily made. The solution of Fick's Law provides the concentration as a function of position and time after release. The distribution of concentration at any instant has the shape of the Gaussian function, being a maximum at the centre and decreasing away from the centre in all directions. The distribution is specified by the maximum value and the standard deviation, the measure of the spread of the distribution. In practice, the cloud is not symmetrical and the standard deviation takes different values in the three coordinate directions. The maximum value and the standard deviations are inter-related by the requirement that the amount of source material in the cloud remains constant and equal to the amount released – called the condition of continuity of species. Information on the standard deviations must be provided empirically. They will clearly depend on the vigour of mixing and thus on the atmospheric stability. Relating the variation of the standard deviations with time to the atmospheric stability is the central problem of passive dispersion prediction.

The concentration distribution for a maintained or continuously emitting source is obtained by integrating with respect to time the distribution equation for an instantaneous source, suitably rewritten for a stationary coordinate system. Again, the standard deviations of the distribution have to be related to the atmospheric stability.

In order to provide a dispersion prediction method that could readily be applied, Pasquill (1961) divided the range of stability into six categories, A to F, ranging from extremely unstable to moderately stable. The stability categories were defined in terms of easily observable parameters – the fractional cloud cover and the windspeed at a reference height of 10 m. The procedure for the estimation of dispersion from a continuous point source was expressed by Pasquill in terms of the angular spread of the cloud in the horizontal direction and the height of the cloud. This was subsequently recast by Gifford (1961), who related these parameters to the standard deviations appearing in the Gaussian model. Gifford presents a set of curves giving the standard deviations as functions of the downwind distance for the six stability categories. These are generally referred to as the Pasquill–Gifford curves and can be found in standard works, e.g. Turner (1970). For an instantaneous point source, a similar scheme was put forward by Beals (1971) but only three stability categories were used because a lack of data prevented a better definition.

An important restriction on this method of estimating dispersion is that the observational basis of the Pasquill stability classification scheme applies to weather patterns similar to those found in England. The problem of classifying

the atmospheric conditions determining dispersion properties has received much attention. Alternative schemes to that of Pasquill have been proposed – see Sedefian and Bennett (1980) for a review of them and a comparison between them. It is now generally accepted that properties more directly related to the turbulence should be used. Methods of estimating turbulence parameters at any latitude have been presented by Holtslag and Van Ulden (1983). Alternatively, direct measurements of turbulence intensities should be used if these are available.

11.8 REVIEW OF RESEARCH PRIORITIES

11.8.1 Introduction

Substantial progress has been made in recent years towards resolving the many issues in assessing dispersion following a chemical accident. The first priority was for reliable data with which to validate and improve mathematical and physical models of dispersion. As a result of several large-scale field trials, mainly in the United Kingdom and the United States, there now exists a very extensive database on the basic case of dispersion of dense gases over flat terrain. The main priorities for further research are in peripheral topics, many of which have already been mentioned in the course of this chapter. In keeping with the separation into formation and dispersion phases adopted earlier, the discussion of research priorities will be similarly separated.

11.8.2 Formation Phase

Theoretical analysis of pool spreading has made good progress but there is surprisingly little supporting experimental information available on this basic fluid mechanics problem. The paper by Webber and Brighton (1984) highlights the variety of phenomena predicted by theory and the scope for physically instructive experimentation.

There is an urgent need for experimental information on sudden releases of pressurized liquefied gases and especially for fundamental measurements of the evolution of the expanding two-phase cloud. Useful laboratory-scale work has been carried out by Bettis *et al.* (1987) but possible scaling effects suggested by Jagger and Kaiser (1981) require investigation at large scale. This is a problem of considerable experimental difficulty and rapid progress cannot be expected. Of particular interest is the case where a jet emission occurs at a height above ground level. Laboratory experiments on the bending over of a dense gas jet by the wind and its return to ground level, as illustrated in Figure 11.1, have recently been reported by Xiao-yun *et al.* (1986). Good agreement

with the predictions of the model of Ooms *et al.* (1974) was found. However, the measurements did not extend to the spreading of the jet over the ground and its subsequent dispersion by the wind. There is also a need for similar experiments on two-phase jets. There is a large range of possible experimental configurations in terms of jet inclination, initial conditions, atmospheric conditions and the scale of release and much work remains to be done.

A feature of experimental work on dense gas dispersion is that each experimental programme adopts its own design of source geometry. Systematic differences between the results of different experiments have been observed and it is suspected that source effects may be the cause. Although these effects might be expected to be unimportant at the distances required for safe dispersion of highly toxic gases, none the less they may be important in some circumstances (and they certainly are important for flammable gases where the dilution to a safe concentration is of the order of 10^2). For example, there are puzzling and substantial differences between plume behaviour as observed in experiments conducted during the Thorney Island programme (McQuaid and Roebuck, 1985) and in ammonia release experiments reported by Koopman *et al.* (1984). In the former, the release was in the form of a gas with negligible initial momentum and in the latter as a flashing two-phase jet with high momentum. Recent wind tunnel experiments by Krogstad and Pettersen (1986) showed that source effects had a strong influence on plume behaviour. Even in the case of fixed volume releases, there has been no systematic investigation of initial aspect ratio effects, a subject of dispute among modellers. There is an urgent need for research to clarify the influence of source conditions.

In practice, the source will in many cases be surrounded by buildings, pipe racks, etc. The effects of release into a building wake have been extensively studied for passive releases but little comparable work has been done for dense gases. Brighton (1986) has speculated on how the approach to the passive case might be adapted to dense gases, while the topic is discussed in the review by Britter (1982). Some of the results of experiments in which a building is located near the source (Krogstad and Pettersen, 1986; McQuaid and Roebuck, 1985) will be relevant.

A release of dense gas may occur within a building, for example within a process building in a chemical plant. The gas is then released to the atmosphere through openings in the building. The effect of this source configuration has been considered by Brighton (1986). The application of a 3-D model to dispersion in the presence of an obstruction has been published by Deaves (1985). However, there is a need for simple guidance on plausible assumptions for the source conditions to use with the simpler types of dispersion model. It is of course desirable that this guidance should be supported by experimental evidence.

11.8.3 Dispersion Phase

The effect of obstructions located away from the vicinity of the source is clear research priority. The emphasis needs to be on the development of simple models, probably limited to some standard types of obstruction. However, it seems likely that for some purposes (e.g. building complexes) it will be necessary to resort to physical modelling. The recent availability of large-scale data will assist the establishment of scaling behaviour and comparative studies have already started (e.g. Davies and Inman, 1987).

Sudden or 'instantaneous' releases have a greater importance in chemical accident studies than in pollution problems. This release mode gives rise to the difficulty that predictions will refer to an average behaviour over an ensemble of releases. The assessor will require guidance on the variability between different realizations of the ensemble in order to put confidence bounds on his predictions (or otherwise to reflect the non-deterministic nature of his predictions). The topic has been considered theoretically by Chatwin (1982) and Carn and Chatwin (1985).

Comprehensive experimental information is lacking although some indication is given in small-scale experiments by Hall *et al.* (1982) that substantial differences (of an order of magnitude) in concentration at a given location can occur for repetitive experiments conducted under the same nominal conditions. The large-scale experiments at Thorney Island showed rather less variability. Davies (1987) has examined the variability exhibited in experiments and in particular considered the problem of assessing variability from datasets that are, for practical and economic reasons, less extensive than required for statistically rigorous ensemble averaging. The quesion of variability is part of the general problem of uncertainty in dispersion estimates. This has been the subject of a recent symposium, of which a summary is given by Carson (1986). In general, there is little firm guidance that can yet be given to the assessor.

The mechanisms of deposition, washout and chemical reaction have received little attention in the context of dense gas dispersion. This is not surprising in view of the poor understanding of these mechanisms in the passive dispersion field. A recent review is given by Underwood *et al.* (1984), while the symposium referred to above concluded that this lack of sufficient understanding is one of the main causes of uncertainty in dispersion estimates. In relation to chemical accidents, some useful theoretical work on the thermodynamics of mixing of ammonia and hydrogen flouride with moist air has been done by Wheatley (1986) and Clough *et al.* (1986) respectively. Field experiments in the United States on chemically reactive gases have been reported by Koopman *et al.* (1984) and further work (e.g. on hydrogen flouride) is planned.

11.9 CONCLUSION

This review has highlighted the variety of problems associated with dispersion following a chemical accident. Available technology allows assessment for many accident situations to be made that are realistic and consistent with experimental evidence. Although considerable efforts have been made in recent years, there remain many problems that require further research. The review has attempted to identify the main priorities. Given the importance attached to the subject as a result of regulatory requirements in many countries, it can confidently be expected that continued progress will be made towards well-founded assessment methods.

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