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THE ROLE OF DENSE GASES IN THE ASSESSMENT OF INDUSTRIAL HAZARDS

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Summary

The paper shows the importance of the problem of the dispersion of dense gas clouds, outlines the several causes of dense gas clouds and considers, qualitatively, their behaviour. Dense gas cloud dispersion should not be considered in isolation. There is a fund of analytical and experimental information available in diverse fields. Finally the need for attention to specific "non-standard" problems is suggested.

Introduction

There has been a marked increase in the industrial use of hazardous materials over the last 10 to 20 years. At the same time there has been a growing concern to develop appropriate regulatory measures, as well as good practices in design and operation so as to achieve an acceptable balance between the economic benefit and the potential or actual harm associated with the use of such materials. Awareness that such harm may involve not only the workers directly concerned in the workplace but also members of the public outside the factory has resulted in a variety of developments in the objectives of industrial safety. The traditional concern to avoid immediate injury within the workplace has now been expanded to encompass, in the extreme case, potential damage from agents that may not manifest their effects for tens or even thousands of years.

Events that have sensitised concern in the U.K. over such hazards include accidents such as those at Windscale in 1957, Aberfan in 1966, and Flixborough in 1974 [1—3]. The accident at Seveso in 1976, the Los Alfaques Campsite propylene tanker fire in 1978, and the Three Mile Island accident in 1979 [4—6] have added to public concern, and there have been numerous other events, perhaps less in the public eye, but of unquestionable significance in shaping the current level of concern. Recognition of the importance of these problems has been evident as the formation of the Advisory Committee on Major Hazards, the public inquiries into developments at Canvey Island and at Windscale [7—11], and the concurrent development of regulations

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governing the operation of sites where large quantities of hazardous materials are located [12]. Numerous industries have at the same time been developing methods of quantifying risks so as to establish a rational basis for control and mitigation.

Quantitative assessment of these risks involves the identification of hazards, the assessment of plant reliability, the estimation of quantities, physical conditions, and likelihood of release of hazardous materials, their subsequent dispersion in the environment and the response of people, structures, etc. exposed to their damaging effects. Whilst it is true that the number of people that have been killed in disasters of this kind is a small fraction of the total number of accidental deaths arising from various causes, such as motoring accidents, social disquiet over the potential for accidents with large numbers of casualties adds extra impetus to the natural desire of industry to prevent such occurrences.

Safety is one of a number of objectives in any industrial enterprise, and resources are consumed in achieving it. This means that priorities must be established, and this can only be done in a responsible fashion if there is an adequate understanding of elements constituting the risk. The release to the atmosphere of hazardous materials that may form mixtures that are denser than the surrounding air is a topic of special concern in this context, for several reasons. First, the fact that they disperse at ground level makes it all the more likely, all other things being equal, that people and structures will be subjected to their effects, as compared with releases of neutral buoyancy or ones that rise due to positive buoyancy. Second, all other things are not equal, since the dispersion behaviour is not so well understood as for neutral or positively buoyant releases, even for the simplest conditions. Third, in reality the conditions are often complicated by such factors as the nature of the release in terms of the failure mode of the containment, whether or not the material was stored under pressure, the production of liquid aerosols, the interaction with building wakes and terrain features, and so forth.

In addition, dense gas mixtures have been involved in disasters such as Flixborough, and records show that materials that may form such mixtures have been released in many of the process industry accidents occurring over the last few decades [5].

Formation of dense gas clouds

The number of materials that may form dense gas clouds is large, but current interest centres mainly on those that are combustible or toxic, with boiling points below ambient temperature. These are commonly stored or transported as liquids, maintained in that phase at or near to their saturation temperature at atmospheric pressure by refrigeration and insulation, or at ambient temperature by pressurisation. A release from such containment to the environment is likely to lead to eventual vaporization of much or all of the liquid. The release may be rapid, as in the case of a catastrophic failure of a pressure vessel, or continuous, as for a release from a pipeline or through a small hole in the vapour space of a pressure vessel. Combinations of these two extremes may occur, as for a spillage of a low boiling point liquid from a refrigerated vessel onto land, in which case there will be an initial rapid boil-off followed by a more steady evolution of vapour at a rate determined by the thermal properties of the ground (assuming that the pool is limited in extent by ground features and does not spread without limit). For spills onto water, the boil-off is expected to be more rapid, since heat transfer takes place more readily, and the pool spread will be over a flat surface [13]. Droplets may be formed and entrained in the vapour released, and these may profoundly affect the density of the mixture. Apart from water droplet formation due to condensation from the ambient air there are several mechanisms that may introduce droplets of the material released:

(1) Bulk-boiling during the vapour-flash in a rapid release from a pressurised container will fragment at least part of the residual liquid into fine droplets.

(2) Droplets may be produced from a boiling pool on land or water due to bursting of vapour bubbles at the surface.

(3) Droplets may be produced by the break-up of liquid jets and sheets exiting at high velocity through narrow openings. The presence and quantity of these droplets has been shown to be crucial in determining whether or not the initial mixture is denser than the ambient air [14].

It is clear from the above that there is a great variety of materials and circumstances of release that may produce dense gas mixtures, and many complicating factors. However, the following broad categories based on material properties provide a framework covering most cases of interest:

(1) Materials having molecular weights less than that of air, but whose vapour at some low temperature of practical importance is denser than ambient air, e.g. methane evolved from refrigerated LNG at its boiling point.

(3) Materials having molecular weights less than that of air, and whose pure vapour at its boiling point is less dense than the ambient air, but which may form dense mixtures due to the presence and subsequent effect of droplets of the material produced by the mechanism of release, e.g. ammonia.

(4) Materials nominally having molecular weights less than that of air, but which may form dense mixtures due to molecular association, e.g. hydrogen fluoride.

Behaviour of dense gas clouds and nature of hazard

In the early stages of a release of dense gas, the behaviour may be dominated by factors arising from the mode of storage, or of release. Continuous releases from pressurised containers may be expected to produce momentum — dominated jets. In the case of catastrophic failure of a pressure vessel there will be a rapid 'vapour-flash' in which a thermodynamically determined fraction of the now superheated (with respect to ambient conditions) liquid converts to vapour. It has been observed that for some materials the violence of this process ejects a substantial fraction of the residual liquid as fine droplets, producing a cloud consisting of a mixture of air, vapour, droplets of the material and of condensed water. There is in this case a substantial initial dilution with air. The overall effect is the rapid introduction of a dense cloud in the ambient flow. Once the initial effects of the stored energy are dissipated the cloud 'slumps' under the action of gravity. Throughout this period the cloud is being diluted further by air entrainment resulting from the action of turbulence in the ambient flow, and turbulence generated by velocity gradients at the interface between the cloud and the surrounding air.

If the cloud is cold then heating from the ground will be of importance, so that the thermal properties of the ground and of the cloud itself will affect the behaviour. As the cloud continues to be diluted, the concentration of the hazardous material continues to fall (though it is important to note that dilution with air will lead to a cooling effect that will compete with heating processes if droplets are present, since the heat for evaporation must come from the cloud). At some level of dilution the density difference will become negligible, and the subsequent behaviour can be described in terms of the dispersion of a release of neutral buoyancy. For the purposes of hazard assessment the object of the dispersion calculation is to determine the potential for damage at various points in the vicinity of such a release. At some distance from the release it is clear that the concentrations experienced will be below those likely to constitute a significant hazard, but within that range the proper specification of the hazard is a complex matter. For flammable or explosive materials it is important to determine the likelihood that ignition will occur if a source of ignition is encountered. Thus one is concerned to know the distribution on a quasi-instantaneous basis of concentrations within the upper and lower limits of flammability (in the percent range) and whether or not these concentrations occur in isolated pockets or in continuous regions stretching over substantial distances, perhaps back to the source. The width of the cloud may well be substantial, so that the hazard needs to be specified in terms of the area affected, which may also extend a significant distance in the upwind direction.

In the case of toxic materials, the levels of concentration above which significant harm may be suffered can be (typically) as low as a few tens or hundreds of p.p.m. (v/v), so that the hazard range may be greater than for flammable or explosive materials.

Although the detailed structure of the concentration distribution is not so critical as for the latter materials, it is not sufficient simply to specify the total dosage or exposure, since for many materials the toxic response does not display a linear trade-off between concentration and duration of exposure. In the case of ammonia, for example, it appears that the response depends on the product of duration of exposure and the concentration raised to some power (about 2.7) [15].

Although dense gas hazards are principally either toxic or explosive (or flammable) in nature, this does not restrict concern only to installations or transport vessels in which they are contained. A release may constitute an external hazard to another type of plant e.g. a cloud of LNG enveloping a nuclear plant would constitute an external explosive hazard. Thus the scope of concern over dense gas hazards includes, to varying degrees, all operations and installations involving the use, manufacture, storage, transport or processing of hazardous materials, be they toxic, explosive or flammable, or radioactive.

It is clear that the requirements of a satisfactory model of dense gas dispersion go far beyond the specification of time-averaged concentration profiles.

Some previous and current related work

Although interest in the dispersion of dense gases is a recent occurrence, problems of a related nature have been evident and studied for some time.

Two principal characteristics of the dispersion of dense gases are

(1) A flow of the gas as a result of an externally imposed velocity field.

(2) A flow of the gas as a result of buoyancy generated forces and pressure gradients.

For both phenomena "flow" is interpreted as incorporating a bulk flow together with the diffusion/mixing/entrainment between the gas and the ambient fluid. The interaction of (1) and (2) provides the complexity of (and interest in) the dispersion of dense gases.

The first characteristic, (1), is the general problem of turbulent diffusion of a passive contaminant, for which an extensive literature exists in both an atmospheric and an oceanographic/inland water context. The velocity field is specified (or determined) and the contaminant is then transported by this field. Several diverse analytical/numerical techniques are available to model this transport. Gradient transfer or eddy diffusivity models abound. Higher order closure models producing mean and fluctuating concentration fields are likely to become more reliable and economical and to be applied routinely for practical pollution predictions in complex flows. The Lagrangian similarity theory is of limited applicability but Taylor's statistical theory for homogeneous flow may be usefully extended to non-homogeneous flows together with single or multi-particle random walk techniques. In addition a large body of data from laboratory and field experiments is available for the flow of a gas as a result of an externally imposed velocity field.

In the early 1960's Turner and several co-workers [16] made extensive measurements of positively and negatively buoyant plumes, typifying characteristic (2), near, and also isolated from rigid surfaces. Their results were interpreted, and analysed, in terms of integral equations and an hypothesized entrainment function. Thus, typically, the density difference between the fluid and its environment led to a bulk motion. The bulk motion resulted in shear, instability and then turbulence and entrainment. The entrainment of the environment into the buoyant fluid retards the bulk flow and provides a self-limiting mechanism. The entrainment function, the ratio of the entrainment velocity to a bulk flow velocity, was further hypothesized to be stability dependent. This approach proved quite successful and suggested considerable generality. More recently, several authors, e.g. see Simpson and Britter [17], have studied in detail the leading edge of the buoyancy induced flow and correlated its velocity with the surface pressure difference across this leading edge. It appears that this leading edge condition may be interpreted as a boundary condition on the rest of the flow. With this interpretation calculations may be greatly simplified. It is also apparent that there are significant differences between the transient motion as controlled by the leading edge and the eventual steady flow.

The interaction between characteristics (1) and (2) is familiar when the plume buoyancy is such that the plume moves away from a rigid surface — the hot chimney plume [18]. In essence the plume rises while being advected by the mean wind field, i.e. a simple superposition of the two characteristics, although this may be carried out by a formal integration of mass and momentum equations together with an entrainment assumption. Of course the same approach is valid for the negatively buoyant plume [19] released from height during its descent, but not upon impingement at the surface.

An interaction between (1) and (2) is also met when a plume of fresh/warm water overrides a saline/cold ambient fluid, e.g. see Fischer et al. [20]. These problems produce bulk flows similar to that observed in dense-gas dispersion problems. The dilution of the plumes is however often quite different — a result of the absence of shear at the free surface as compared with a rigid surface.

Several other active areas of research impinge on the problem of the dispersion of dense gases. For example consider the generation of anabatic/katabatic winds.

When a slope is either heated or cooled, changes in the density of the adjacent fluid will generate a flow, up a heated slope and down a cooled slope. At night the downslope flows converge at the valley floor and drain away down the valley. Early analyses reduce to a determination of eddy diffusivities. Numerical solutions are hindered by uncertainty about the physical processes involved. In a recent analysis Manins and Sawford [21] use an extended hydraulic approach, i.e. allowing entrainment of the ambient fluid into the denser downslope flow. The solution is obtained by introducing the stability-dependent entrainment function of Ellison and Turner. Their approach emphasizes the importance of mixing between the katabatic flow and the environment as the essential retarding mechanism of the flow. In a comparison field study Manins and Sawford [22] confirmed that the surface stress was unimportant at a slope of 4.5°. Their study also showed the importance of three-dimensionality of the flow. Cold air from the lateral slopes converged to enhance the main flow.

A useful fund of field and analytical work on katabatic flows in complex terrain will result from the ASCOT program of the U.S.D.O.E., e.g. Gudiksen [23], and become generally available in the next few years. The analytical models should be applicable (after suitable modification) to problems of dense gas dispersion in complicated topography.

Further examples of density-driven flows and their interaction with an ambient velocity field are to be found in the extensive literature existing on sea/lake breezes, thunderstorm outflows, turbidity current on slopes, fjord and reservoir dynamics and in the general oceanographic literature. Included within this last example is the development of surface mixed layers resulting from surface cooling or an applied wind stress. Many of the classic experiments on entrainment, e.g. Kato and Phillips [24], have been set in a mixed-layer development context.

Further model developments

Analytical and numerical model development continues along two distinct lines. The simpler approach is based on the solution of integral equations. This does not necessarily imply that the mean velocity and concentration profiles are top-hatted, only that the non-uniform profiles are to be represented by similarity profiles and integral variables. These models, though limited, have only a small number of adjustable constants whose effect may be easily interpreted physically. These constants are determinable from, and should be checked against, simple laboratory and field experiments. The second approach is based on solutions of the relevant differential equations simplified by the introduction of eddy diffusivities. These models are far more flexible than those based on integral equations, however they suffer from considerable uncertainty in the specification of the eddy diffusivities. For example few models stress that the Reynolds analogy (the equivalence of mass, heat and momentum eddy diffusivities) is not valid when the flow has a stable density-stratification. In addition, it is important to remember that in many problems of turbulent diffusion the use of eddy diffusivities is regarded as out-dated and appeal to higher-order closure models is made.

There is also much fundamental work being done (and to be done) which will guide model development and experiment design. For example Rottman and Simpson [25] have shown that a fixed volume release of dense fluid will result in a raised leading edge to the cloud (containing a major part of the cloud's mass) when the container has a top to it. If there is no top to the container, no raised leading edge is observed. Of course, field experiments with a moving ambient are further complicated by a "horse-shoe" vortex around the cloud and the source structure.

Nevertheless with the many models presently available, the existence of nearly a decade's worth of laboratory experiments in several facilities and the increasing availability of field results, the time is opportune for the assembly of a "work-book" similar to those existing for the dispersion of passive contaminants. Such a "work-book" would, presently, have wide uncertainty limits, but still provide a useful initial screening technique, particularly for users considering a more detailed investigation.

It is apparent that much effort has been expended in the study of dense gas dispersion under the constraints of flat terrain, constant surface roughness and very long fetch with no obstructions. Models available now or in the near future will, presumably, provide acceptable estimates of hazard distances under these conditions. At worst the models will be a useful correlation of available field and laboratory experimental data.

Several "non-standard" problems will soon require a great deal more attention than they now receive.

Two limiting aspects of topographic influence are when the scale of the topographic feature is large or small compared with the scale of the released volume. When the topographic feature is large compared to the scale of the released volume, the topography reduces to the local slopes. Ellison and Turner [26], Britter and Linden [27] and Beghin, Hopfinger and Britter [28] have analysed and experimented upon continuous, starting and instantaneous line plumes on slopes in the absence of ambient winds. Similar work needs to be extended to point/area sources in a moving ambient. When the scale of the topography is small compared with the released volume, then the dense gas may flow around (or over) the topography and be diluted in the wake. A similar problem has recently been studied by Snyder, Britter and Hunt [29] in the context of pollutant dispersion in stably stratified environments and in the context of elevated inversions impinging on topography. Further situations that may be of interest are the flow of a plume over a two-dimensional topographic feature, e.g. a wall or a shoreline, and the release of a dense gas within a three-sided topography, e.g. a quarry, with the ambient flow into the quarry.

Clouds of dense gases are "pancake-shaped" not rising very far from the ground. They are, therefore, quite likely to be advected through forests or areas of vegetation which may be as tall or taller than the height of the cloud. The resulting dilution and reduction in advection speed require study particularly as a forested area may be a useful safety feature for both dispersion and detonation purposes.

A further area of uncertainty is how to incorporate the influence of local buildings in existing and future models. When the release volume is, or has become, large compared to the scale of the buildings then the buildings might be treated as an increased roughness. Such an approach has proved useful for releases within an industrial complex.

Many releases will be directly into the wake of either a building or the ruptured container and the scale of the released volume may be comparable to or smaller than the building scale. The interaction of the released volume with an isolated building leads both to an increased dilution of the release and a "hold-up" within the wake of a building converting an instantaneous source to a time-varying one. A semi-empirical theory would suggest that mixing in the wake of a building of height H and width D would increase the depth of a continuous plume by Δh

where $$\frac{\Delta h}{H} \alpha\, C_D \left(\frac{U^3 D}{Qg'}\right)$$

where C_D is a relative drag coefficient, U the on-coming velocity and Qg' the negative buoyancy flux from the source. Whether the dilution in the wake of buildings might be treated by such an approach or by locally increased diffusivities in a first-order closure (eddy diffusivity) model is a question that requires attention.

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