SAFE DISPOSAL OF RELIEF DISCHARGES

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The treatment of the stream, possibly containing hazardous gas, liquid and solid components, released from a chemical reactor, following a runaway reaction, is discussed, hopefully in a logical manner. Possible hazards resulting from an untreated release are reviewed and their mitigation by dispersal, containment, inertial separation, scrubbing and combustion considered. Attention is directed to sources of information on design methods and the solution of ancillary problems.

Keywords. Emissions (hazardous); dispersion (atmospheric); containment (of emissions); gas cleaning; incineration; flaring

INTRODUCTION

The engineering of chemical reactor relief disposal was reviewed by Mark Kneale in the last symposium in the present series (1). The subject of the safe handling of dangerous or objectionable emergency releases is however wide and of some complexity. It seems worthwhile, therefore, to continue the discussion, emphasising some aspects that had to be passed over lightly by Kneale and taking advantage of some more recent publications that are relevant. A full treatment of the subject is beyond the scope of a symposium paper and it seems that there may be a case for a hand book giving detailed guidance on decision-making and design. Such a hand book does not appear to be generally available at the present moment.

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LEGISLATIVE AND OTHER BACKGROUND

Section 5 (1) of the Health and Safety at Work etc. Act 1974 places upon persons having control of prescribed premises in the United Kingdom the duty to use the best practicable means for preventing the emission to the atmosphere of noxious or offensive substances or of rendering them harmless or inoffensive (2).

Insofar as such substances are the product of a runaway reaction, the best practicable means of preventing their emission must be through reaction monitoring and control. Prior hazard analysis should reveal the ways in which control may be lost and the steps necessary to avoid such loss or to regain control once lost. It is prudent nevertheless to provide additional safety in the shape of controlled release to atmosphere, unless of course the results of the runaway reaction can be totally contained. Some aspects of reaction control and controlled release have been considered in this Symposium and elsewhere. The latter step can however give rise to problems related to that part of the law that calls for the emission to be rendered harmless or inoffensive. Let us first consider those respects in which a chemical reactor discharge might be deemed to be harmful or offensive.

In the first place, the discharge may be flammable. In the form of gas, vapour or fine droplets it will form an envelope around the point of discharge in which concentrations are between the limits of flammability. These have values measured in units of per cent by volume, but see ref (3) for specific figures. This cloud is liable to ignition with resultant flame formation and pressure effects dependent upon its situation and extent. An emission at elevated temperature may self-ignite, depending upon the spontaneous ignition temperature value. See ref (3) for data. The deposition of liquid drops will give rise to a hazard of fire, which may well be widespread.

In the second place, the discharge may be toxic. Since toxic limits of vapours are usually orders of magnitude less than lower flammability limits, a toxic cloud is characteristically of much greater extent than a flammable cloud. Toxic particulates will deposit to produce possibly harmful environmental effects, the larger sizes being gathered around the source of discharge and the smaller sizes further afield.

Toxic limits are less well-defined than those of flammability. This is partly due to lack of information, but more fundamentally due to the effect of time of exposure upon what is an acceptable concentration. The most extensive and readily accessible data relate to what are known in the U.S.A. as "threshold limit values" (4) but are now referred to in the U.K. as "exposure limits" (5). These are essentially acceptable concentrations in the workplace for the duration of the eight-hour working-day, although "short term exposure limits" have been recognised in some cases, to relate to short, ten-minute exposures. Neither of these relates precisely to the exposure of a person at some distance from an emergency discharge of limited duration, yet they provide a basis for consideration and judgment.

Corrosive discharges will usually cause the greatest damage, both to persons and to property, through the deposition of drops in the near field. Corrosive gases and vapours can cause more widespread, but usually more superficial damage to sensitive materials.

Offence under the rather ill-defined heading of "nuisance" may be caused most widely of all. This includes odour, for which the threshold limit is often well below the toxic limit, and noise. Since emergency discharges are characteristically short-lived, it may be concluded that the nuisance problems should not loom large in comparison with those associated with periodic or continuous releases.

A reason for treatment of an emergency discharge with which the law is not concerned is the recovery of material of monetary value. Against this value will have to be set not only the cost of retaining the value-containing discharge, but also the cost of separating from the retained material the component of value.

TREATMENT STRATEGY

A consideration of the nature of a likely emergency discharge on the above lines can provide the basis for decision as to an appropriate procedure for acceptable disposal. First however, the available methods should be mentioned, leaving until a later stage their more detailed consideration. The basic methods are :

1. Direct discharge to atmosphere, under conditions leading to rapid dilution
2. Total containment, either in the reactor itself or in a connected vessel, or vessels, ultimate disposal being deferred to a convenient time
3. Partial containment, followed by the separation of particulates, basically by inertial (gravitational and centrifugal) methods; and the extraction of gaseous or finely-divided suspended pollutants by scrubbing or other "active" methods
4. Combustion in flares or incinerators and discharge of the (less objectionable) combustion products to atmosphere.

With a sufficient outlay on capital expenditure and operation, including notably, maintenance, almost any degree of clean-up of emergency discharges is possible. The precipitating event should however be infrequent and this circumstance greatly influences the extent to which the expenditure is worthwhile. It is in considering this question that the value of effective reaction control becomes particularly apparent. If the conclusion indicated by process hazard analysis is that an emergency release should be very infrequent, a lack of complete clean-up, or even no clean-up at all may be suggested by consequence analysis as being tolerable. If on the other hand the discharge is seen to be unavoidably frequent and/or the consequences of an untreated release unacceptable, the alternatives are total containment or a sophisticated clean-up system. The former will probably be the more cost-effective, especially if a number of independent reactors can share a common facility.

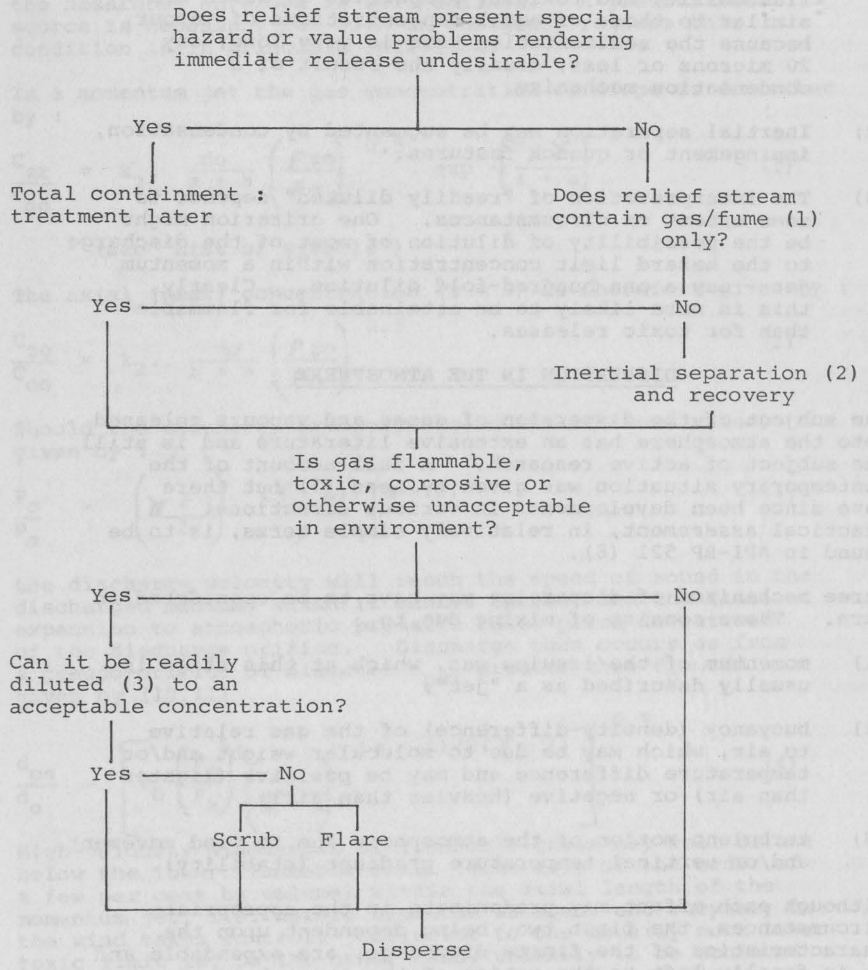
If particulates of a significant settling velocity are likely to be discharged, gravitational separation (knock-out) is both practicable and desirable. This is a necessary prelude to atmospheric release of a discharge that is otherwise unobjectionable, or to its destruction by flaring because large particulates, either liquid or solid, will not be completely burnt in the flare. An incinerator, however, would be expected to be more tolerant. Toxic and nuisance particulates down to say 10 microns may be separated by centrifugal (cyclonic) methods, the range being extended by the inclusion of impingement features, or by the incorporation of water quench, although the latter has the disadvantage of requiring commissioning when the emergency release occurs. The same requirement arises with the use of condensers or recirculatory scrubbers, although these may be essential for the removal of highly toxic gases.

The recovery of discharged materials of value will generally be accomplished by total containment, although if they are wholly or mainly in particulate form, inertial separation will probably be cheaper. Least desirable are wet methods, since a further separation step then becomes entailed.

For final discharge of gas to atmosphere, advantage may be taken of height and vertical momentum to assure acceptable ground level conditions. Avoiding a falling-off to a low rate of discharge may be desirable from several points of view - to minimise the total release to atmosphere and/or the amount of material needing to be recovered; and loss of vertical jet momentum at the point of ultimate release. Overall strategies for minimising the release are illustrated and discussed by Thomas (6).

A decision tree simplified from one presented by Kneale (1) is shown in Fig. 1. Any such statement is bound to need reservations, but a systematic approach is to be advocated. Notes are attached to the Figure regarding the meanings of "fume" and "readily diluted".

FIG.1 - DECISION TREE



Notes to Fig. 1 -

(1) "Fume" refers to a fine particulate suspension, the flammability and toxicity properties of which are similar to those of equal concentrations of vapour, because the sedimentation time is very long; say 20 microns or less, usually the result of a condensation mechanism.

(2) Inertial separation may be augmented by condensation, impingement or quench features.

(3) The interpretation of "readily diluted" depends to some extent on circumstances. One criterion might be the possibility of dilution of most of the discharge to the hazard limit concentration within a momentum jet - say a one hundred-fold dilution. Clearly, this is more likely to be attainable for flammable than for toxic releases.

DISPERSION IN THE ATMOSPHERE

The subject of the dispersion of gases and vapours released into the atmosphere has an extensive literature and is still the subject of active research. A full account of the contemporary situation was given by Lees (7) but there have since been developments in various directions. A practical assessment, in relatively simple terms, is to be found in API-RP 521 (8).

Three mechanisms of dispersion may have to be considered in turn. These consist of mixing due to :

(1) momentum of the issuing gas, which at this stage is usually described as a "jet";

(2) buoyancy (density-difference) of the gas relative to air, which may be due to molecular weight and/or temperature difference and may be positive (lighter than air) or negative (heavier than air);

(3) turbulent motion of the atmosphere due to wind movement and/or vertical temperature gradient (stability).

Although each effect may predominate in the appropriate circumstances, the first two, being dependent upon the characteristics of the finite discharge, are expendable and it is finally left to the motion of the atmosphere to complete the process of dispersion. Before that stage is reached however, dilution of the discharge to below the hazardous (flammable or toxic) limit may have been achieved. It is necessary therefore to consider, in turn, the criteria by which momentum and buoyancy mixing become ineffective for practical purposes. This is considered at some length in a series of papers by Marshall (9), which treat also the deposition of particulates and include numerical examples.

In high-velocity discharges momentum jet mixing predominates. For hazardous discharges it is desirable to make as much use as possible of this mechanism since dilution is rapid and the hazardous envelope is well-defined. A pressurised source is necessary but with an emergency release this condition is in principle fulfilled.

In a momentum jet the gas concentration envelope is described by :

$$\frac{C_{zr}}{C_{oo}} = k_2 \cdot \frac{do}{z + a} \left(\frac{\rho zo}{\rho o} \right)^{0.5} \cdot \exp - \left(\frac{k_3 \gamma}{z + a} \right)^2 \qquad (1)$$

(see "List of symbols")

The axial (peak) concentration ($\gamma = 0$) is therefore given by :

$$\frac{C_{zo}}{C_{oo}} = k_2 \cdot \frac{do}{z + a} \left(\frac{\rho zo}{\rho o} \right)^{0.5} \qquad (2)$$

Should the discharge pressure exceed the critical value, given by :

$$\frac{P_o}{P_a} = \left(\frac{\gamma + 1}{2} \right)^{(\gamma + 1)/(\gamma - 1)} \qquad (3)$$

the discharge velocity will reach the speed of sound in the discharged medium, which it cannot exceed, and the final expansion to atmospheric pressure takes place downstream of the discharge orifice. Discharge then occurs as from a pseudo-orifice of diameter d_{ps}, greater than d_o, and given by (10,11)

$$\frac{d_{ps}}{d_o} = \left[C_D \left(\frac{P_o}{P_a} \right) \left(\frac{2}{\gamma + 1} \right)^{(\gamma + 1)/2(\gamma - 1)} \right]^{0.5} \qquad (4)$$

High-velocity discharges of flammable gases may well dilute below the lower flammable limit (generally of the order of a few per cent by volume) within the axial length of the momentum jet, i.e. before momentum is spent and buoyancy or the wind takes control. Dilution to the usually much lower toxic limit is, on the other hand, unlikely to be achieved by momentum alone. In any event, an accidental discharge will usually slow down as pressure in the relieved vessel falls and momentum will fail to achieve safety unaided in the later stages of the discharge unless measures are taken to cut off the release before the vessel pressure has dropped too much. This may be achieved by a re-seating relief-valve, although the reliability of such a device is not high.

A typical study of the effect of decaying vessel pressure on the ground level concentration resulting from the release of a heavier-than-air toxic gas, using Marshall's methods of calculation, is described by Binns and Barrett (12).

CONTAINMENT

As pointed out by Kneale (1), the ultimate method of containment is to design the reactor to withstand any foreseen temperature and pressure rise. He suggests the use of risk analysis to arrive at a cost-effective relationship between the design stress and the probability that the maximum conditions will actually be experienced. In this situation only small thermal and overfill relief would be provided.

The subject of the total containment of emergency releases in a separate vessel is dealt with very fully from the point of view of design by Speechly, Thornton and Woods (13) and from the operational standpoint by Welding (14). Taken together the two papers reflect many years of practical experience.

Once again, cost-effectiveness has to be considered in view of the large and costly vessel usually required for total containment. Where a number of independent, but similar reactors have to be served, a shared containment vessel will reduce the relative cost and may be justified on the grounds that simultaneous discharges from more than one reactor are improbable if the reactors are truly independent. Steps must be taken to ensure that there is no interaction between individual emergency relief devices, e.g. bursting discs, that would result in a spurious release closely following a genuine one. These and many other matters, including containment vessel sizing and working pressure, inert gas provision, venting and drainage, and reaction forces upon the reactor-containment system, are carefully considered by Speechly et al (13).

A partial containment system designed to provide hold-up while cooling and cleaning hot flammable gases released from polyethylene reactors under runaway conditions is described by Martinot (15). Such an arrangement can avoid explosive self-ignition of the discharge, which is liable to be a problem with such reactors. The author also describes simpler forms of quenching device, not involving the partial containment provision, which serve a similar purpose, although probably less reliably.

SEPARATION

The separation of suspended matter from a discharge may, in the first instance, be effected by inertial techniques. The gravity settler, or knock-out pot, has the advantage of low pressure-drop. The principle of design is to equate the sedimentation time with the time of residence. This leads to a bulky vessel and the inability to separate the smaller particulates.

The design of knock-out pots, principally as a prelude to flaring, is detailed in API-RP 521 (8). The treatment by Grossel (16) is more relevant to reactor discharges and covers a variety of unit types ranging from an open-topped blow-down vessel, through the simple enclosed horizontal blow-down drum, the vertical drum with tangential inlet and the fully-developed cyclone separator, to separators in which separation forces are augmented by water wash-down. Impingement features may also be incorporated in cyclone separators (17).

The design of an inertial separator demands a knowledge of the gas feed rate and of the particle size distribution of the suspended matter. The design of the reactor relief provision implies a knowledge of the former. In an emergency release it will usually peak and then fall off considerably. The peak may be "shaved" by providing containment capacity upstream of the separator. Lower feed rates may be avoided by arranging to cut off the discharge below a certain reactor pressure. This is also a desirable provision to maintain final exit velocities and to minimise the total release of material, as pointed out elsewhere in this paper.

Particle size distribution may be difficult to predict, but the separation system can be designed to remove efficiently particles above a certain size, which is usually equivalent to removing those more environmentally objectionable and also those that cannot be satisfactorily destroyed in a flare.

After a preliminary separation of large particles by inertial methods, a condensation stage may be used to develop the smaller particles before further separation either by inertial methods or by scrubbing. As an alternative to the last, the stream may be sent to an incinerator or flare stack. If large general-purpose scrubbing or combustion facilities are available, problems of commissioning and of overloading are reduced.

Further clean-up of the discharge stream from the finer particulates, possibly augmented by condensation, may be undertaken by scrubbing. At this stage, gaseous pollutants may also be absorbed, either by solution in water or by reaction with an aqueous solution of an appropriate reagent. The necessary contact may be organised in scrubbers of the packed column, plate column or venturi types. The design of scrubbers, and of condensers is adequately dealt with in standard chemical engineering hand books and text books.

The combustion products of some pollutants are less objectionable than the pollutants themselves. In these circumstances the discharge, after preliminary clean-up, may be fed into a pre-existent furnace or flare system. This may introduce other hazards against which precautions have to be taken, such as suck-back of air due to condensation and flash-back through flammable mixtures. Combustion products may be corrosive and thermal radiation and noise problems may arise from flares. Their design is treated fairly fully in API-RP 521 (8) and other information is available elsewhere (18). A recent development is in the use of the Coanda effect to improve efficiency of combustion, as reported by Kaldair (19). Gas incinerators are dealt with by Bonner (20)

Sophisticated techniques for the highly efficient cleaning of gases and for the treatment of high-temperature discharges are available (21). These relatively costly methods will not generally be appropriate to rarely-occurring emergency releases.

VENT STACKS

Unless the gas for discharge to atmosphere is innocuous, or is expected to be so by reason of the clean-up provisions applied, the vent stack should be designed to give non-hazardous conditions at ground level. If the hazard is of flammability, the purpose may be achievable through a sufficiently high vertical velocity at the outlet, so that dilution is completed by momentum exchange. With toxic discharges however, ground level safety is much less likely to be secured by outlet velocity alone and height of the outlet above grade is likely to be necessary. In either event, a high (but subsonic) outlet velocity is desirable and API-RP 521 (8) suggests 500 $ft.s^{-1}$ (150 $m.s^{-1}$) at maximum discharge pressure. As already illustrated, the effect of falling discharge pressure must be considered and possible steps taken to avoid the consequences, for example by automatically cutting off the discharge when the pressure peak has passed.

A relief valve or orifice across which the pressure ratio exceeds the critical value for a sonic discharge will operate as a sound generator. API-RP 521, pp. 61-63 (8) considers the situation where a vent stack is directly attached to such a discharge and gives a method of estimation of noise intensity as a function of distance from the stack tip.

If the vent stream is flammable, ignition at the stack outlet is a possibility and the consequences in terms of thermal radiation will have to be considered. This subject has attracted much attention in connection with flares and the ignition of continuous or prolonged vent discharges. There are numerous publications but there is not complete unanimity regarding recommended methods of calculation of radiation intensity. Emergency reactor releases are short-lived in principle and it may be concluded that only short-term exposure limits have to be avoided.

If there is the possibility of the admission of air to a flammable vent stream, the hazard of flash-back of an ignited vent stream must be considered. At the end of a discharge of light gas, air may enter the stack and produce a similar situation.

DESIGN OF PIPING AND SUPPORTS

Guidance on the sizing of piping in connection with disposal systems is given in API-RP 521 (pp. 44-49) (8). Reference is made to thermal shock and stress, and to drainage requirements. Transient pressure forces during the discharge are fully discussed by Woods and Thornton (22) with an illustration involving the reactor boundary, bends and a deflector plate. The resultant forces have to be accommodated not only in the design of the piping and equipment, but also in their supports. The importance of the latter point is underlined, with a number of illustrations, by Chambard (23).

LIST OF SYMBOLS

a = axial displacement of notional source (m.)

C = concentration of emitted material (vol.fraction)

C_D = discharge coefficient

d = diameter of jet (m.)

P = pressure, absolute (bar)

z = vertical upward distance (m.)

r = radial distance (m.)

ρ = density ($kg.m^{-3}$)

γ = ratio of specific heats of gas

Subscripts

a = ambient atmosphere

o = initial

ps = pseudo

Constants (recommended by Long)

	For time-mean concentration	For instantaneous concentration
k_2	6	9
k_3	5	2

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