

Figure 4: Effective depressuring rate assuming the homogeneous equilibrium model of Tangren et al (1949) over depressuring rate based on assumed choked flow of gas (isentropic). As x-axis the gas quality.

SAFE DISPOSAL OF REACTIVE CHEMICALS FOLLOWING EMERGENCY VENTING

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This paper will discuss the technical issues that must be resolved and the options available for reducing the potential of a major release following emergency venting. The results of a recent research programme funded by the Health and Safety Executive on coping with the relief of reacting systems will be presented. From this work, equations for the design of containment systems to cope with two-phase releases of reactants will be described and their application to different chemical systems illustrated.

runaway reactions, venting, calorimetry, two-phase flow, disposal, quenching, containment, emergency relief, exothermic reactions

1. DISCUSSION OF PROBLEM

1.1 INTRODUCTION

The sizing of a suitable relief device is quite complex when the overpressurization problem is caused by a runaway reaction. The rate of pressure and temperature rise is often difficult to obtain and relief actuation frequently leads to venting of a two-phase mixture of vapour (or gas) and liquid. The subject of relief for runaway reactions was studied by DIERS (Design Institute for Emergency Relief Systems) in the USA, (Fisher, 1985). As a consequence of the DIERS work, relief sizing for runaway reactions is now quite well understood and safe designs can be completed economically.

The objective of relieving a process unit is simply to prevent damage due to overpressurization. The disposal of the vented fluids is a separate matter and was not studied in the DIERS project. This paper will focus on design implications of venting into disposal tanks, either with a view to complete containment or followed by relief into a downstream unit (flare, absorber, incinerator etc). The use of small scale testing to provide the necessary information and the application of the information will be illustrated with examples.

1.2 RELIEF OF RUNAWAY REACTIONS - OVERVIEW

Almost invariably, the pressure rise in process equipment is due to the generation of vapour (or gas). For example, if fluid in a closed vessel undergoes exothermic reaction producing heat at a rate Q (W) then the rate of vapour generation M (kg/s) is given by (Q/λ) where λ (J/kg) is the latent heat of vaporisation.

In order to correctly size relief for a runaway reaction, it is necessary first to classify the system according to the types of reaction products and their ability to remove heat during venting. The same considerations are also very useful in the design of disposal systems.

Vapour Pressure Systems

Vapour systems are those where the system pressure is equal to the vapour pressure of the liquid. In such cases, the reactant will be cooled (due to the latent heat) as vapour is vented; at a sufficiently high vent rate, the heat of reaction can be balanced by the cooling effect, resulting in 'tempering' of the reaction where no further temperature rise occurs. Since the pressure and temperature are directly related, the pressure will also cease to rise at this point.

Gassy System

Gassy systems are those where the system pressure is due entirely to the presence of non-condensable gas, rather than the vapour pressure of the liquid. The gas is normally the product of decomposition. In these mixtures, venting of the gas produces no noticeable cooling because the gas has no latent heat. As a result, the reaction temperature continues to rise during venting; pressure can only be arrested by ensuring that the gas is vented at a sufficiently high rate. Thus, unlike vapour systems, the pressure is controlled (and reduced) without cooling the reaction.

In these systems the rate of reaction governing the vent size will clearly be much higher than when the vent opens.

Hybrid and Complex Reactions

There are many reactions which do not conform to the simple classifications above and therefore need to be considered differently. One common deviation is systems that have a significant vapour pressure and at the same time produce non-condensable gases - often referred to as hybrids. The behaviour of such reactions during venting depends on the relative contributions to pressure of the vapour and non-condensable gas.

The specific data needed to size vents depends on the reaction type: vapour pressure, gassy or hybrid (Duxbury and Wilday, 1989, Singh 1990).

1.3 LIQUID CARRY-OVER DURING VENTING

A major reason for concern over venting of reactants to atmosphere is that liquid can be entrained with the vented vapours. In the worst case, not uncommon in many instances, virtually the entire reactor contents may be emptied. It is important to determine when this may happen so that downstream equipment may be suitably selected and designed.

2. ALTERNATIVES TO ATMOSPHERIC VENTING

The considerations in determining the choice of safety system between venting to atmosphere, venting into an external vessel and possibly not venting at all, are safety and cost. The traditional method, venting directly to atmosphere, poses an environmental hazard and possibly a toxic and/or explosion risk to on-site workers and the neighbouring community. However, this method is simple, generally reliable and frequently inexpensive.

The main alternatives to this approach are:

- (a) elimination of the need for venting by making process control or other operating changes which prevent the incident from occurring
- (b) elimination of the need for venting by containing the worst incident within the reactor
- (c) elimination of venting by injection of an inhibitor or quench fluid into the vessel after runaway reaction is detected or, cooling to remove the heat produced by active cooling.
- (d) disposal of the reactants to another vessel containing a quench fluid or providing a similar facility that avoids release of chemicals to the atmosphere.

The above options are not possible for every system and in each case they present different advantages and disadvantages. The first option, essentially avoidance by design, is frequently the most favoured but not always possible in practice. The effort required to establish the acceptability of this option is quite large.

Containment of the worst credible incident by designing for the maximum pressure, option (b), is only possible in limited cases. Frequently, runaway reactions can lead to extremely high pressures (over 50 bar say) and therefore containment may be very expensive. One attractive consideration is to combine (a) and (b), that is, use better control and operating procedures to 'dilute' the worst credible case and thereby make containment more viable.

Active addition of a fluid that prevents propagation of an incident, option (c), can be extremely effective if properly designed. Acceptance of this option depends firstly on whether a suitable inhibitor can be located and secondly whether a sufficiently reliable system can be designed.

The final option, venting into an external disposal tank is the reverse of the previous system. The crucial difference is that the protective system is largely passive and so much less likely to fail, provided of course that it is properly designed and maintained.

The disadvantage is that the hardware may be more elaborate and possibly more expensive. The present paper is concerned with the last option, disposal into external equipment. The above alternatives and the most important features of each are summarized in table 1.1.

3. SPECIFICATION OF DISPOSAL UNITS : THEORETICAL

3.1 STEPS INVOLVED IN SPECIFICATION

Disposal systems (or containment vessels) may be considered as being either open (atmospheric

pressure units) or closed (high pressure units). Closed systems must invariably contain some quench fluid, else the reaction will not be suppressed, while atmospheric drums may be either empty knock-out drums or, vessels containing a quench fluid.

In general the following design options are available:

- . Closed (pressure) drum with quench fluid
- . Open (atmospheric) drums with quench fluid
- . Open (atmospheric) drum without quench (i.e. simple k.o. drum).

The design considerations will differ not only according to the above options but will also depend on the reaction type. A division which is helpful, is to consider gassy reactions separately from vapour pressure (tempered) type particularly when empty, atmospheric drums are considered.

There are broadly three assessment stages to consider after initiation of relief, with different parameters being relevant at each stage:

Stage 1 : Initial rapid dump out of Reactor

- . equilibrium temperature in drum
- . vapour/gas generation from drum
- . downstream liquid carry-over check

Stage 2 : Subsequent Reaction within Disposal drum

- . reaction rate
- . vapour/gas generation rate
- . liquid carry-over check

Stage 3 : Final conditions in Disposal drum

- . maximum temperature
- . maximum pressure

Continued reaction in disposal drum (stage 2) should be eliminated by design where possible so that the reaction stops after entering the disposal unit.

In this paper, detailed consideration will be limited to reactions that exhibit vapour pressure system characteristics.

3.2 SPECIFICATION OF INITIALLY EMPTY DRUM (VAPOUR PRESSURE TYPE REACTION)

3.2.1 Flash Vaporisation

A vapour pressure system will be vented when the chemicals are above their atmospheric boiling point (by definition). If the mixture vents as a two-phase froth, the liquid will cool from the reactor temperature T_r down to the atmospheric boiling point T_b . The energy available due to

this cooling will vaporize some of the liquid, the weight fraction x of liquid ending in the vapour phase.

This may be calculated from (if x is small):

$$x = \frac{C_r (T_r - T_b)}{\lambda} \quad (3.1)$$

where C_r is specific heat of the liquid and λ the latent heat of vaporisation.

Since the relief temperature T_r is normally known, the important variable is T_b ; this is frequently difficult to calculate because the reactor composition at the point of relief is not known. The best method for estimating T_b is experimental.

If venting rate from the reactor is W (kg/s), then the initial rate of vapour generation due to flash vaporisation will be:

$$\dot{M}_f = Wx \quad (3.2)$$

The vapour from the reactor will normally be negligible compared with \dot{M}_f and so may be neglected.

3.2.2 Vapour Generation Due to Continued Reaction

If the temperature T_b is high enough to sustain continued reaction in the disposal drum further vapour must be vented from the drum. The maximum vapour rate from this source will occur when the drum contains the most liquid. This may be approximated $m_0(1-x)$ giving the following expression for the maximum vapour generation rate due to chemical reaction, \dot{M}_r :

$$\dot{M}_r = \frac{m_0 (1-x) C_r (dT/dt)_d}{\lambda} \quad (3.3)$$

where m_0 is the total mass of reactants and $(dT/dt)_d$ is the equivalent self-heat rate in the drum (at temperature T_b). This rate of vapour generation will occur when the disposal drum is at its highest level (i.e. reactor is empty). Thus the total vapour rate from the drum will be:

$$\begin{aligned} \dot{M}_{\max} &= \dot{M}_f + \dot{M}_r \\ &= \frac{WC_r (T_r - T_b)}{\lambda} \left[1 - \frac{m_0 C_r (dT/dt)_d}{W\lambda} \right] + \frac{m_0 C_r (dT/dt)_d}{\lambda} \quad (3.4) \end{aligned}$$

The important parameter needed in the above equation is $(dT/dt)_q$; ideally, it should be obtained experimentally.

In summary, the vapour rate from the drum will initially be given by equation (3.2) and will rise to a maximum given by equation (3.4). After this, the venting period is complete and so the rate will be just M_r as obtained from equation (3.3).

3.3 SPECIFICATION OF OPEN PASSIVE QUENCH DRUM

3.3.1 Initial Quench Temperature

Unlike open disposal drums where the temperature in the drum is determined by the physical properties of the reactants, this parameter is selected by the designer in the case of quench drums. The selection is based on two simple criteria:

- the reactants must be cooled sufficiently to bring the reaction under control; this depends entirely on the reaction kinetics
- condensable vapours from the reactor should be successfully condensed; this generally requires that the quench drum temperature must be at least 10°C lower than the condensation temperature of the vapour.

Thus, the amount of quench fluid necessary for a particular application depends on the final temperature T_{qf} required within the vessel. The relevant parameters can be calculated by performing a heat balance on the quench liquid and the vented reactants.

This leads to:

$$m_q = \frac{(T_r - T_{qf}) m_o C_r + x m_o \lambda}{C_q (T_{qf} - T_o)} \quad (3.5)$$

where m_q is the amount of quench fluid (kg), T_{qf} is the final temperature in the quench vessel (°K), T_o is the initial temperature of the quench fluid (°K), C_q is the specific heat of quench fluid (J/kg °K).

3.3.2 Gas Flow Out of Drum

Air Displacement

The first impact of venting into the quench drum will be to displace the air above the quench fluid; in order to maintain a low pressure in the drum, this must be rapidly removed. The air displaced will equal to the volume of liquid condensed. If the venting rate is W (kg/s) and this has a density of ρ_r (when condensed as liquid) then air displacement rate (kg/s) is given by:

$$\dot{M}_{qa} = \left(\frac{\rho_a}{\rho_r} \right) W \quad (3.6)$$

where ρ_a is the air density. This air will be saturated with the quench fluid and with the reactants vented. If the vapour pressure of the quench fluid/reactants at the maximum drum temperature is $P_v(T_{qd})$ (in bar), then the amount of vapour in the air will be:

$$\dot{M}_{qv} = \dot{M}_{qa} \left(\frac{P_v(T_{qd})}{1.013} \right) \quad (3.7)$$

Thus the total of air plus vapour displaced from the quench drum will be:

$$\begin{aligned} \dot{M}_{qd} &= \dot{M}_{qv} + \dot{M}_{qa} \\ &= \left(1 + \frac{P_v(T_{qd})}{1.013} \right) \left(\frac{\rho_a}{\rho_r} \right) W \end{aligned} \quad (3.8)$$

Continued Reaction in Quench Drum : Vapour Pressure System

In addition to the simple physical displacement of air, there may also be continued reaction in the drum despite the cooling and dilution by the quench fluid. Evaluation of this rate differs between gassy and vapour pressure type reactions.

The rate of reaction in the drum will be negligible at the start of venting and reach a maximum when all the reactants have been quenched. (The drum temperature will be the maximum at the end and the concentration highest). The effect of continued reaction only becomes significant if the temperature in the drum increases from T_{qf} to the atmospheric boiling point of the mixture, T_{qb} .

The maximum that may actually be reached T_{qm} may be estimated from:

$$T_{qm} = T_{qf} + \left(\frac{m_o}{m_o + m_q} \right) \Delta T_r \quad (3.9)$$

where $\Delta T_r = (T_{em} - T_r)$, T_r being the reactor temperature at relief point and T_{em} the maximum exotherm temperature. Thus ΔT_r represents the adiabatic temperature rise.

If $T_{qm} > T_{qb}$, then clearly the maximum temperature will be limited to T_{qb} the boiling point and the vapour rate needs to be determined. If $T_{qm} < T_{qb}$ then further calculation is not needed since the mixture never reaches boiling point and vaporisation will be quite small.

If the reaction rate at temperature T_{qb} is equivalent to a self-heat rate of $(dT/dt)_q$, then the amount of vapour produced (provided $T_{qm} > T_{qb}$) is:

$$\dot{M}_{qr} = \frac{dT/dt_q (m_q + m_o) C_r}{\lambda} \quad (3.10)$$

This is equivalent to equation (3.3) for an open knock-out drum. The drum outlet pipe will be sized to accommodate \dot{M}_{qr} plus \dot{M}_{qd} , thus preventing pressure or temperature rise.

3.3.3 Temperature and Pressure Variations in Drum

The quench drum temperature will increase from the initial cold value (T_o) to the maximum T_{qm} . If reaction continues, the temperature may increase T_{qm} , unless this exceeds to the boiling point of the mixture, T_{qb} , in which T_{qb} will be the maximum. The pressure should remain close to atmospheric.

In order to prevent the temperature rise above T_{qr} , reaction must be completely suppressed; this is particularly important in the case of gassy reactions.

3.4 SPECIFICATION OF CLOSED PASSIVE QUENCH DRUM : VAPOUR PRESSURE SYSTEM

3.4.1 Initial Quench Drum Temperature

The initial quench drum temperature following relief is given by the following heat balance:

$$T_{qf} = \frac{r [T_r C_r + x \lambda] + C_q T_o}{r C_r + C_q} \quad (3.11)$$

where $r = m_o/m_q$. Using this equation, the reactant/quench mixture temperature can be calculated for any quantity of quench fluid. The vapour mass fraction, x , is frequently quite small (< 0.05).

3.4.2 Final Quench Drum Temperature due to continued Reaction

The above temperature (T_{qf}) represents the drum conditions at the end of the venting phase; continued reaction will increase this.

The final temperature is determined by the enthalpy still remaining in the vented reactants. This can be determined from a knowledge of the heat of reaction, ΔH_r .

The enthalpy already consumed is proportional to the temperature rise at the point of venting, compared with the maximum (adiabatic) available rise. This ratio is, β ,

$$\beta = \frac{T_r - T_i}{\Delta T_{ad}} \quad (3.12)$$

(T_i is initial temperature at which the exotherm in the reactor started, and ΔT_{ad} is the adiabatic temperature rise). The fraction of energy remaining in the reactants is $(1 - \beta)$. An enthalpy balance gives:

$$T_{qm} = \frac{C_r \Delta T_{ad} (1 - \beta) r}{\bar{C} (1 + r)} + T_{qf} \quad (3.13)$$

where \bar{C} is the mean specific heat of the reactant/quench liquid mixture. Note that $C_r \Delta T_{ad}$ is equal to the heat of reaction, and $(1 - \beta)$ is the fraction of this energy still available.

3.4.3 Final Quench Drum Pressure

The pressure P_m generated in a closed quench drum is given by:

$$P_m = P_{air} + P_v$$

where P_{air} is the pressure of the air in the drum and P_v the vapour pressure of the quench/reactant mixture. The value of P_v depends on the maximum temperature T_{qm} determined from the above equation. The air pressure results from the compression that takes place as the reactants enter the quench drum. This can be calculated as follows.

If the volume of the quench drum is V and the initial void fraction α_o , then the volume of air is $\alpha_o V$ and the volume of quench liquid $(1 - \alpha_o) V$. The final air pressure P_{air} from an initial pressure P_o is:

$$P_{air} = \left[\frac{1}{\alpha_o} - \frac{1 - \alpha_o}{\alpha_o} \left(1 + r \frac{\rho_q}{\rho_r} \right) \right]^{-1} P_o \quad (3.14)$$

where ρ_q is the quench fluid density. Thus, unlike the vapour pressure component P_v , the air pressure depends on the quantity of quench fluid in relation to the amount of reactants (ie r) and the initial void fraction in the drum.

3.5 CHECK FOR LIQUID CARRY-OVER

3.5.1 Types of Chemical Systems

A crucial feature of disposal unit design (except for closed quench systems) is to ensure that vented liquid is not carried over from the disposal vessel. Clearly, this possibility exists because the same phenomenon leads to carry-over in the first place out of the reactor.

The behaviour of most chemicals can be divided into three categories:

- naturally 'foamy' systems where virtually all the liquid is carried out with vapour, even at quite low vapour velocity
- all gas vapour venting systems, where full disengagement of the vapour and liquid occurs leaving no liquid carry-over
- intermediate systems where the liquid level at the point of venting and the vapour velocity through the vessel determines whether liquid will be carried over. This system frequently fits a 'bubbly' or 'churn-turbulent' model of two-phase flow; 'bubbly' characterized chemicals are closer in behaviour to the foamy type system while the churn-turbulent is further towards all gas/vapour venting system.

Whether proper containment in an open disposal drum takes place depends on the design, in relation to the above categories. In the case of foamy systems, an open disposal tank would not be appropriate unless the reaction could be effectively quenched (hence no gas/vapour flow out of the quench drum). A more likely situation is a chemical system fitting the churn-turbulent two-phase behaviour. In such cases, liquid carry-over can be avoided by detailed evaluation of the vessel design in relation to the physical properties of the vented chemicals.

The type of behaviour that may be expected in any situation can only be established from practical experience, either in the plant or experimentally.

3.5.2 Check for Liquid Disengagement

If the gas or vapour is to be separated from the incoming liquid in a knockout drum, the velocity \dot{V} through the drum to prevent liquid entrainment must satisfy:

$$\dot{V} \leq K \sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \quad (3.15)$$

where $\dot{V} = Q_g / (\pi D^2/4)$, Q_g = gas flow rate out of drum (m^3/s), D = drum diameter (m), ρ_L = liquid density (kg/m^3), ρ_v = vapour density (kg/m^3), K = empirical constant; for vertical drums $K \sim 0.03$ to 0.05 .

The most important parameter is Q_g , which is calculated from experimental data.

When the chemicals have been found to entrain significant amounts of liquid with gas or vapour, the above equation is invalid.

As an example presence of two-phase (vapour-liquid) flow is assured provided the following inequality holds based on the churn-turbulent model (Leung 1987):

$$M_v \geq \frac{2\alpha_o U_\infty A_x \rho_v}{(1-\alpha_o)} \quad (3.16)$$

where M_v = vapour flow (kg/s), α_o = initial void fraction in drum, U_∞ = bubble rise velocity in reaction mixture (m/s), typically 0.2 to 0.5 m/s , A_x = drum cross-sectional area.

Application of (3.16) to any system will show whether two-phase flow will occur. If it does, two basic steps can be taken to prevent this:

- increase the vessel cross-sectional area (hence reduce vapour velocity)
- increase the free-board (α_o).

It should be emphasised that in order to apply the above equations, it is necessary first to establish the presence of two-phase, churn-turbulent flow through the reactor. This normally requires experimental work, which will be discussed later.

3.6 INFLUENCE ON UPSTREAM EQUIPMENT (REACTOR/VENT)

The installation of disposal equipment can be expected to affect the reactor that is being vented. It is necessary to establish that the interaction is acceptable and that it will not lead to an unsafe vent size. In practice, this requires that the vent flow rate should not be significantly decreased as a result of the disposal unit installation.

4. ROLE OF BENCH-SCALE TESTING

4.1 BASIC REQUIREMENT

Experimental testing plays a very important role in both the understanding of runaway reactions, and the design of related safety features such as relief vents and disposal facilities.

The types of instruments useful for relief sizing (and by suitable extension also for disposal unit design) have features in common with devices used for hazard screening but also aspects that are rather special. Most instruments are based on the principle of adiabatic calorimetry. This ensures that when a sample undergoes exothermic reaction (leading to an increase in temperature) that heat is not lost from the sample. In addition to heat loss, another important feature is the heat retained by the sample container. The thermal capacity of small sample cells used experimentally can be quite large compared with that of the sample: the net effect is the same as heat loss to the environment. Data for relief system design needs to be free of this effect so that rates of temperature and pressure rise are representative of full scale plant.

The instrument used in the present study was PHI-TEC II (Singh, 1989) shown in figure 1. This uses a test cell of around 120 cm^3 made of very thin walled metal (to reduce the thermal mass). This is surrounded by three electrical guard heaters whose temperature is controlled through a computer to match the sample temperature. In addition, a pressure compensation system is employed which exerts a N_2 pressure on the outside of the test cell to match the pressure increase due to reaction.

When relief devices have to be extended to include downstream disposal, the adiabatic calorimetry objective must be extended to the disposal unit. Also, the extended unit must use test cells of low thermal capacity. Thus, in order to study relief of runaway reactions and their disposal, it becomes necessary to have two somewhat similar adiabatic units directly connected. The original runaway reaction can then be initiator in one unit and then, at the appropriate point, vented into the disposal cell. The latter may contain a quench fluid for example, and so the reaction of the mixture can be studied.

The disposal unit used in this study is shown in figure 2 and fits onto a standard PHI-TEC II unit.

The vented reactants from the reaction cell are flashed into a similar container, the disposal cell, which is placed between its own guard heaters. Two pipes (normally 1/8" diameter) are fitted to the cell, one is connected to the vent pipe from the reaction cell and the other acts as a vent pipe and also as the pressure transducer connection. These pipes should be heat traced. Disposal cell may be up to 2.5 times that of the reaction cell.

The objective of the disposal unit is to allow the assessment of suitable external containment systems for reactive chemicals vented in an emergency. Tests provide sufficient data firstly to decide on the type of containment system feasible and secondly to evolve a detailed specification.

5. SIZING OF OPEN CONTAINMENT DRUMS (PHENOLIC RESIN REACTIONS)

The first example illustrating the combined use of the theoretical equations and test equipment is the manufacture of phenolic resins. The basis used for the illustration will be a reactor of volume 4.54 m³, containing 3628 kg of reactants which is vented at about 121°C. The vent rate needed for such a system is about 150 kg/s (Leung, 1986). The objective of this example is to show how the reactants could be contained in a disposal drum which is open to the atmosphere.

5.1 CLOSED SYSTEM PHENOLIC REACTION TEST

The production of phenolic resins involves the reaction between phenol and formaldehyde using a suitable catalyst, typically an acid or base. The reactions are extremely exothermic and can runaway out of control. The results (pressure and temperature against time) of a caustic initiated reaction (formaldehyde to phenol molar ratio 3.2) are shown in figure 3. The reaction was initiated by heating up to 40°C in a closed test cell in the PHI-TEC II apparatus. The maximum temperature reached is 187°C and maximum pressure 20 bar.

5.2 VENTING TESTS WITH PHENOLIC REACTION

In subsequent tests, the phenolic reaction was vented into the disposal unit (see figure 2) at about 120 - 125°C after initiation in the test cell within PHI-TEC. First, the disposal cell was empty, simulating a simple atmospheric dump tank; this was then repeated by venting into cold water.

The pressure and temperature data from the first of the two disposal tests is given in figure 4. This shows the same sort of rise as in figure 3 and then a sudden drop in both pressure and temperature when the relief valve was opened. The relief occurred at 123°C (3.6 bara). The corresponding data from the disposal cell is shown in figure 5; the temperature and pressure were initially both constant at ambient conditions. At the point of relief, the temperature undergoes a very sharp rise as the hot reactants are vented.

Recall that the disposal cell was open to atmosphere at this point - hence the pressure does not rise immediately (in fact it drops marginally as air was forced out). When the disposal cell was "closed in", the temperature starts to rise steadily, as does the pressure. The rate of temperature rise is approximately 1.5°C/minute.

Note that the temperature in the reaction cell was 123°C at the point of venting but it flashes down to 90°C in the disposal cell, this being the atmospheric boiling point of the flashed mixture. The rate of temperature rise in the disposal cell is also low compared with the reaction cell - 1.5°C/minute compared with approximately 12 to 15°C/minute. This can be clearly seen in figure 6, where the reactor and disposal cell data is compared.

The amount of material collected in the disposal cell was measured at the end. Approximately 73g (out of 80g in the reaction cell) were vented.

In the second disposal test the reacting mixture was vented into a disposal cell containing 25g of water (compared with 80g of reactant). The other difference was that the disposal cell was not open to the atmosphere - it was closed at all times. The corresponding disposal (quench) cell data is shown in figure 7. The temperature rises rapidly to about 64°C (from 30°C) and the pressure increases to 1.8 bara. No subsequent increase in pressure and temperature was observed (the cell was under adiabatic conditions). The point of relief was the same as in the last test, 123°C (3.6 bara). At the end of the test, it was found that 41.8g of the reactants were vented into the quench cell.

5.3 CHECK FOR LIQUID CARRY-OVER

It is possible to check the likelihood of two-phase flow out of a reactor by rapidly venting the reactants through a large vent to induce a high vapour velocity through the test cell. Such a test with 80g of sample showed that the amount of liquid remaining in the cell was about 41g; thus approximately 70% of the cell was empty. This shows that two-phase relief does occur. However, since the test cell did not completely empty (or certainly not down to 5-10%), there is some vapour-liquid disengagement. The so-called "churn-turbulent" two-phase regime is suggested by the results.

5.4 PHENOLIC DISPOSAL SYSTEM : SIMPLE KNOCK-OUT DRUM

5.4.1 Gas/vapour rate from drum

Design of a simple atmospheric knock-out drum, possibly connected to a flare or other suitable disposal unit, requires only an estimation of the amount of gas/vapour that leaves the drum.

The reactants are vented from an elevated pressure at 123°C down to atmospheric pressure. This will cause some vapour to be generated as the liquid cools to its atmospheric boiling point. Using the experimentally determined value of $T_b = 90^\circ\text{C}$, equation (3.1) gives:

$$x = \frac{2900 (122 - 90)}{2502 \times 10^3} = 0.037$$

($C_p = 2900 \text{ J/kgK}$, $\lambda = 2502 \times 10^3 \text{ J/kg}$, from reference Leung, 1986). Therefore, only 3.7% of the liquid is vaporized. In addition to this, some vapour will come over with the liquid from the reactor. This is usually quite small. For example, if 90% of the vented fluid (by volume) is vapour, then the fraction by weight is approximately 0.013.

Therefore the total fraction of vapour entering the disposal unit is approximately (0.037 + 0.013) i.e. 0.05. For the example being considered, the venting rate from the reactor (W) is 150 kg/s, hence the amount of vapour generated is from (eqn. 3.2) $\dot{M}_r = 0.05 \times 150 \text{ kg/s} = 7.50 \text{ kg/s}$.

The tests show that reaction will continue in the drum after venting; the vapour produced by continued reaction in the drum must be included. This may be based on the self-heat rate in the drum, found to be 1.5°C/minute experimentally. The amount of vapour produced by this, based on total reactor mass is (eqn 3.3):

$$\dot{M}_r = \frac{3628 \times (1.5/60) \times 2900}{2502 \times 10^3} \text{ kg/s} = 0.105 \text{ kg/s}$$

Therefore, the total amount of vapour is:

$$\begin{aligned} \dot{M}_{\text{max}} &= \dot{M}_r + M_r \\ &= (7.50 + 0.105) \text{ kg/s} = 7.605 \text{ kg/s} \end{aligned}$$

The density of the vapour at 2.0 bar and 120°C is 1.2 kg/m³ as quoted above (based on Leung, 1986). At 90°C and atmospheric pressure this will become $\rho_v = 0.65 \text{ kg/m}^3$. Therefore the volumetric flow of vapour is:

$$Q_g = \dot{M}_{\text{max}} / \rho_v = 11.7 \text{ m}^3/\text{s}$$

5.4.2 Knock-out Drum Size

If the above vapour is to be separated from the incoming liquid, a knockout drum must be provided. The velocity V through the drum to prevent liquid entrainment must satisfy (eqn 3.15).

The most important parameter in this equation is Q_g , which was calculated above from experimental data. This gives a vertical drum diameter $D = 3.16 \text{ m}$.

The drum height (or length) must ensure that liquid entrainment from the drum does not occur. This will now be considered.

5.4.3 Check for Two-phase Flow

The above method for knock-out drum sizing is based on the assumption that vapour-liquid separation methods experienced in general petrochemical practice, are applicable. Test work with the phenics reaction shows that it is susceptible to liquid entrainment. It is therefore necessary to check that the drum will not permit liquid carry-over with the vapour.

The presence of two-phase (vapour-liquid) flow is assured provided the following inequality holds based on the churn-turbulent model (established earlier) using equation (3.16). This shows that if the drum diameter of 3.16m, is maintained, the liquid level must not exceed 0.35 (i.e. $\alpha_0 = 0.65$) to ensure all vapour flow. This corresponds to a drum volume of about 12m³.

Similarly, if the diameter is say 6m, the cross-sectional area increases (velocity reduced) so that all vapour flow is produced only with a 2/3rds full drum ($\alpha_0 = 0.33$); this is equivalent to a drum volume of about 6m³.

5.5 DISPOSAL SYSTEM : PASSIVE QUENCH

The crucial variable in this case is the amount of quench fluid that is necessary. This in turn is determined by the safe temperature determined for the quench plus vented fluid. In the test programme, a temperature of 60°C was found to be safe. Somewhat higher temperatures may also be acceptable but this is a matter of optimization. Certainly, 80°C would be the maximum acceptable since the condensation temperature of the vented fluid (based on test 3) is around 90°C. Hence 60°C is quite close to the optimum.

It is possible to calculate the amount of quench fluid needed by using equation 3.5. The most important parameter in this equation is T_{qf} , the safe final temperature and this has been obtained directly from the test. Inserting a value of 3628 for m_0 in equation 3.5 gives $m_q = 6507 \text{ kg}$.

Thus, the quench tank would need to be large enough to contain (6507 + 3628) kg of liquid. Allowing for vapour space at the top of the vessel, a tank volume of approximately three times the reactor volume would be needed, say 14 m³.

6. DESIGN OF TOTAL CONTAINMENT SYSTEM (METHANOL-ACETIC ANHYDRIDE)

In this second example, the sizing of a total containment quench drum will be illustrated. For comparison, an open quench drum will also be illustrated. In order to permit comparison with the phenolic resin example, the same reactor volume and similar venting conditions will be used.

6.1 CLOSED CELL RUNAWAY REACTION TEST

The reaction considered in this case is the exothermic esterification of methanol by acetic anhydride. The reaction has been studied extensively both as an example for relief sizing (Gibson et al., 1987, Singh 1989) and for disposal (Singh and Boey, 1991).

The methanol-acetic anhydride reaction occurs at ambient temperature, the rise in pressure and temperature against time is shown in figure 8. This relates to a methanol to anhydride molar ratio of 2. Characteristically, the reaction commences very slowly at first but then rises rapidly, reaching a maximum pressure of about 15 bara and a maximum temperature 175°C.

6.2 VENTING TESTS

Venting into Empty Cell

The disposal tests were carried out by initiating the venting (from the reaction cell in PHI-TEC) at about 115°C. The vented reactants, under adiabatic conditions, flashed down to 72°C but still showed a self-heat rate of 12.5°C/minute. Thus, though the reactants cool substantially after venting down to atmospheric pressure fairly high reaction rate persists; cooling of the reactants is clearly necessary.

Two tests were carried out to investigate the effect of different quantities of water on the vented reactants. The results obtained (with M_w = mass of water and M_r = mass of reactants vented) are given in table 7.1. As the ratio of vented reactants to water is reduced, the initial mixture temperature and self-heat rate become lower. The results from the second of these tests are shown in figure 9.

Test	M_w (g)	M_r (g)	M_r/M_w	Initial mixture temp (°C)	Self-Heat rate (°C/min)
3	29	51	1.76	63	4.0
4	41.3	52.6	1.27	53	3.1

TABLE 7.1 : Effect of Quench on Reaction Rate

6.3 DISPOSAL SYSTEM DESIGN BASIS

The methanol-acetic anhydride reaction is clearly extremely hazardous, reaching a maximum pressure of about 15 bara and temperature 175°C at a maximum self-heat rate of over 87°C/minute. Relief of the reaction into an empty, atmospheric disposal tank from an initial temperature of about 115°C would result in a temperature of only 72°C; this confirms the result previously reported (Singh and Boey, 1991). The two quench tests provide information on the effectiveness of quenching with water. Using 0.56kg of water per kg of reactants produces a mixture temperature of 63°C and a self-heat rate of 4.0°C/minute. If the dilution is increased to 0.79kg per kg of reactants, then temperature is reduced to 53°C and the self-heat rate is 3.1°C/minute.

Clearly, even a high degree of dilution does not prevent the mixture from continuing to self-heat. This is to be expected since the reaction occurs at ambient temperature.

A characteristic of the system is that it vents as a homogeneous two-phase vapour/liquid mixture. This was used as the basis for relief sizing in previous studies of this system (Gibson, 1987). For this reason experimental verification has not been carried out.

6.4 DISPOSAL INTO ATMOSPHERIC KNOCK-OUT DRUM

The reactants are vented from an elevated pressure at 115°C down to atmospheric pressure. This will cause some vapour to be generated as the liquid cools to its atmospheric boiling point. The weight fraction of the vented liquid that will vaporize, given by (eqn. 3.1), is 0.08.

Thus, a large fraction of the chemicals will leave an atmospheric drum as vapour. In addition, considerable amount of liquid will inevitably be entrained. Clearly therefore, atmospheric venting into an empty knock-out drum is not an acceptable option.

6.5 DESIGN OF PASSIVE QUENCH DRUM

6.5.1 Safe Design Basis

The results of the disposal tests show that extremely large quantities of quench water would be needed to prevent continued reaction in the quench drum.

The most practical approach is therefore to select a pressurized drum. The pressure generated in the quench drum will be the vapour pressure of the reactant/water mixture plus the air pressure. The first of these components, vapour pressure, depends on the maximum temperature in the quench drum following relief; this may be calculated from equation (3.16).

Assuming a water temperature (T_w) of 25°C and reactant temperature (T_r) of 115°C, the values in table 7.2 are obtained for the mixture temperature (T_{qm}) following venting. The final temperature T_{qm} (i.e after exothermic reaction) from an initial temperature T_{qr} is given by equation (3.13). (The adiabatic temperature rise, ΔT_{ad} , is (178 - 25)°C, i.e. 153°C).

r	T_{qr} (°C)	T_{qm} (°C)
1.0	55.5	87
1.5	64.0	101.8
2.0	70.6	112.6
2.5	75.5	120.5
3.0	79.5	126.8
3.5	82.8	131.8

TABLE 7.2 : QUENCH MIXTURE TEMPERATURE AS A FUNCTION OF DILUTION

6.5.3 Maximum Quench Drum Pressure

The air pressure (eqn 3.14) and maximum pressure (i.e including vapour pressure P_v) for different values of r (reactant to water ratio) and α_v (initial void fraction in the drum) (assuming $\rho_w/\rho_r \sim 1.25$) are given in table 7.3. The P_v contribution is based on values of T_{qm} at different values of r in Table 7.2.

r	P_{air} (bara)			P_m (bara)		
	$\alpha_o = 0.6$	$\alpha_o = 0.8$	$\alpha_o = 0.9$	$\alpha_o = 0.6$	$\alpha_o = 0.8$	$\alpha_o = 0.9$
1.0	5.9	1.45	1.16	6.65	2.2	1.91
1.5	-	1.90	1.26	-	3.0	2.36
2.0	-	2.67	1.38	-	4.77	3.48
2.5	-	4.57	1.53	-	7.57	4.53
3.0	-	16.0	1.71	-	19.6	5.31
3.5	-	-	1.94	-	-	6.14

TABLE 7.3 : MAXIMUM DISPOSAL DRUM PRESSURE

6.6 SELECTION OF QUENCH DRUM DESIGN

6.6.1 Closed System Containment

The previous disposal design study was based on a hypothetical reactor charge of 3,628 kg; this will also be used as the basis in this case. Table 7.2 shows that a moderately low pressure disposal drum can be installed in order to quench the methanol-acetic anhydride reaction. The drawback (as will be seen) is that the size of vessel needs to be rather large.

The relief set pressure of the reactor is about 3.5 bara - the disposal drum pressure must be lower than this. In order to minimize the influence of back-pressure (in the drum) on the venting process, the drum must permit almost uninterrupted relief. This can be achieved by ensuring that the drum pressure is low enough to allow choked flow from the reactor. The pressure ratio needed for this is about 0.9 for flashing two-phase flow; a ratio of say 0.8 would therefore be acceptable. This gives a maximum drum pressure of 2.8 bara.

Looking at table 7.3, this pressure limitation could be satisfied by the following options:

- (a) $r \sim 1.25$, $\alpha_o \sim 0.8$
 (b) $r \sim 1.7$, $\alpha_o \sim 0.9$

Since the mass of reactants to be vented is 3,628 kg the first option requires a water quantity equal to $(3628/1.25)$ kg, i.e. 2902 kg, say 3m^3 of water. Therefore, the drum volume must be $3/(1-0.8) = 15\text{m}^3$. Similarly for the second option, the water quantity needed is 2134 kg and the drum volume about 21m^3 . Clearly the first option is to be preferred as it leads to the smallest drum. (Trial and error may produce a more optimal solution).

Therefore, approximately 3000 kg of quench water in a 15m^3 drum would be acceptable.

6.6.2 Atmospheric Pressure Drum

The above considerations apply to a closed disposal drum design. A low pressure drum, open to the atmosphere is feasible provided the maximum temperature in the unit can be kept below the boiling point. This temperature will be between 72 and 100°C depending on the relative

amounts of water and reactant : as the water quantity is increased, the boiling point rises but the maximum temperature goes down. From table 7.2, a dilution factor (r) of below 1.5, gives a vapour pressure below 1.1 bar. Hence, $r = 1.0$ for example (vapour pressure 0.75 bar), would be acceptable. In this case the amount of water required is $(3628/1.0)\text{kg}$, i.e. 3628 kg, say a drum volume of 10m^3 allowing for some void. This is considerably less than the 15m^3 for a closed drum.

The open drum design will not of course totally contain the organic vapours. The air in the drum will be displaced and may be assumed to be saturated with the vented chemicals. This may be acceptable in many instances particularly if the air line can be taken to a safe location.

7. CONCLUSIONS

The release of large amounts of toxic chemicals from reactors undergoing runaway reaction has been the cause of major industrial accidents. In this paper, the emergency venting of such reactors into external containment systems, rather than to atmosphere, has been described in terms of the physical and chemical processes that occur. The design of suitable disposal units and the derivation of necessary data has been exemplified by reference to two reacting systems, phenolic resin polymerization and an esterification.

Using a common basis of a reactor of volume 4.54m^3 vented at about 120°C , the following results are obtained:

REACTION	CONTAINMENT SYSTEM		COMMENT
	TYPE	SIZE	
PHENOLIC	Open Knock-out Drum	D = 3.16 m V = 12 m ³ D = 6 m V = 6 m ³	Approx. 5% of reactants will flash as vapour
	Open quench drum	V = 14 m ³ Quench water ~ 6.5 m ³	Small loss of vapour
ESTERIFICATION	Open quench drum	V = 10 m ³ Quench water ~ 3.6 m ³	Small loss of vapour
	Closed quench drum (Pressure ~ 3 bara)	V = 15 m ³ Quench water ~ 3 m ³	No vapour loss

It is concluded that practical solutions can be obtained for the difficult problem of containing vented runaway reactions. A combination of simple analytical expressions and pertinent small-scale data can be used to explore the range of possible options and generate an optimal solution.

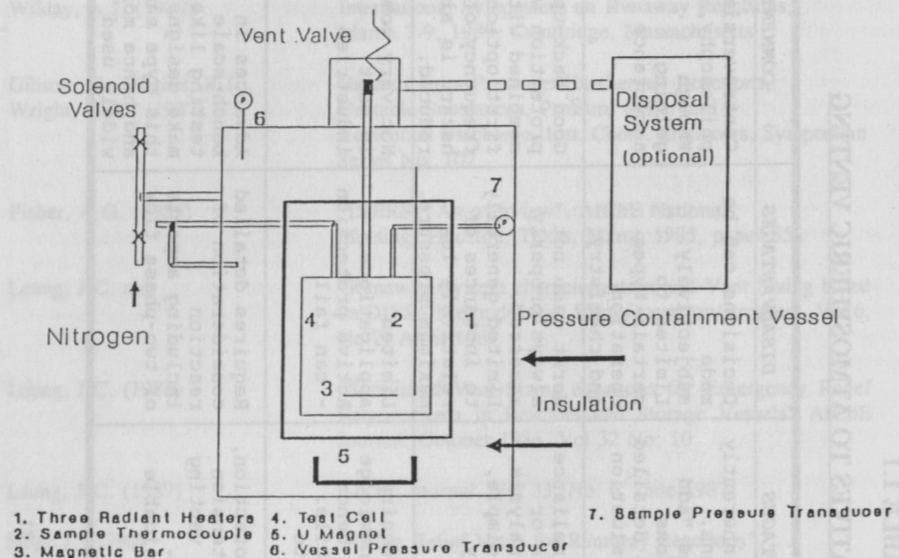
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TABLE 1.1
SUMMARY OF MAIN ALTERNATIVES TO ATMOSPHERIC VENTING

ALTERNATIVE	DESCRIPTION	ADVANTAGES	DISADVANTAGES	COMMENTS
Eliminate hazard by control	Make control and/or operating changes that reduce incident frequency to an acceptable level	Produces inherently safe designs. Discourages "add on" solutions. Encourages detailed process evaluation	Decisions can be made subjectively. Limited to certain types operation and chemistry	Controversial philosophy, though gaining acceptance
Contain Pressure	Design pressure vessel such that it will contain the worst incident	Places no reliance on controls or detailed analysis. Extremely simple, potentially reliable	Worst case not always properly assessed. Limited generally to instances of relatively low maximum pressure.	Good back-up protection when combined with the first option, frequency of hazard is also reduced.
Inject inhibitor into reactor (Dousing)	Trigger injection of a reaction inhibitor to stop runaway before it can do damage	Does not require detailed knowledge of cause - hence very versatile. Can be quite expensive	Limited applications. Active protection - can fail	Not very common in most industries
Dispose into external tank	Vent reactants into suitable knock-out drum or quench tank followed by flaring, incineration etc.	Passive protection, natural extension of present venting philosophy. Widely applicable	Requires detailed consideration of reaction including aspects of two-phase flow	Advances in bench-scale testing likely to make designs of this type easier and hence more widely used

The PHI-TEC Calorimeter for the Assessment of Reactive Materials



- 1. Three Radiant Heaters
- 2. Sample Thermocouple
- 3. Magnetic Bar
- 4. Test Cell
- 5. U Magnet
- 6. Vessel Pressure Transducer
- 7. Sample Pressure Transducer

FIG.1

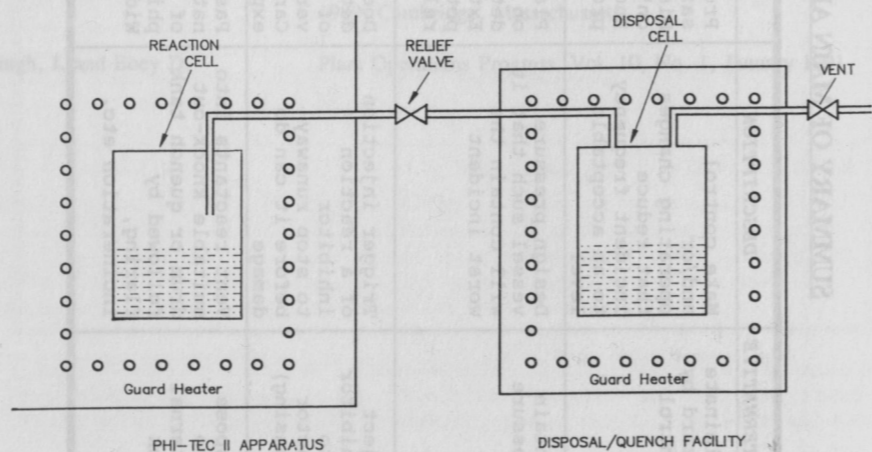


FIGURE 2 BENCH-SCALE DISPOSAL CELL CONNECTED TO PHI-TEC APPARATUS

FIG 3 : NaOH CATALYSED PHENOLIC REACTION PRESSURE & TEMPERATURE Vs TIME

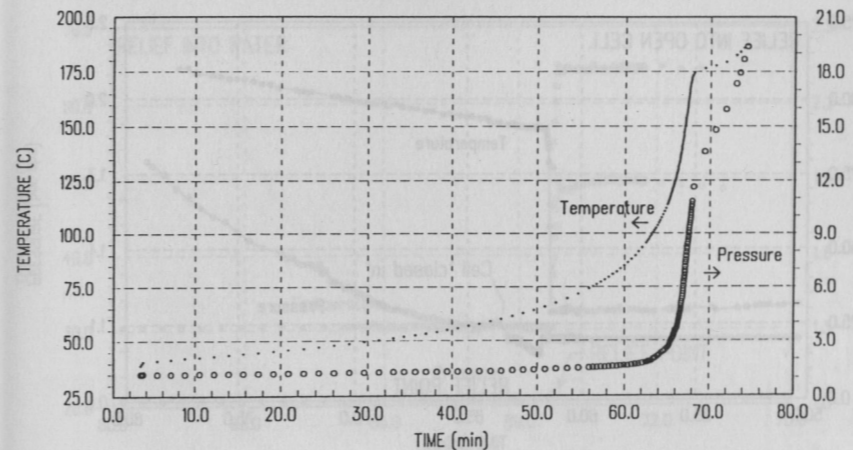


FIG 4 : RELIEF OF NaOH INITIATED REACTION PRESSURE & TEMPERATURE Vs TIME IN REACTION CELL RELIEF INTO EMPTY TANK

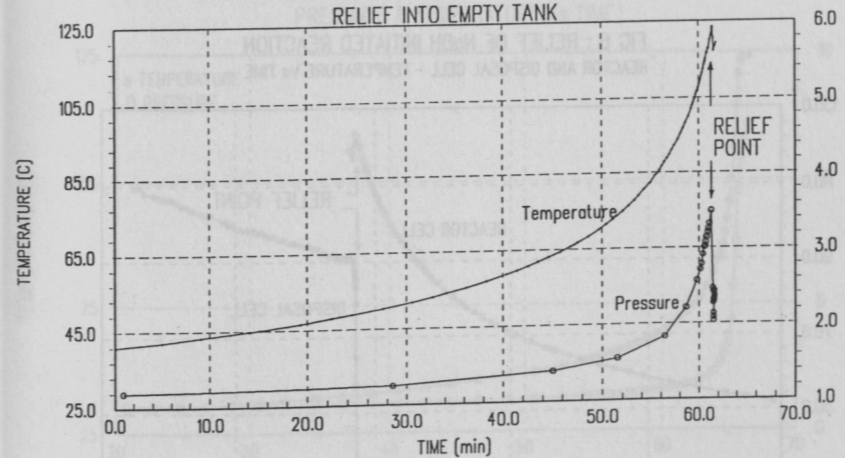


FIG 5 : RELIEF OF NaOH INITIATED REACTION
PRESSURE & TEMPERATURE Vs TIME IN DISPOSAL CELL

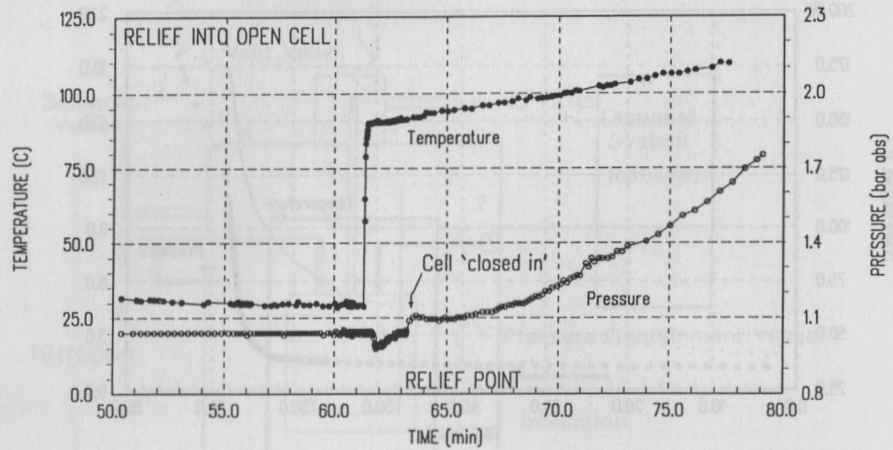


FIG 6 : RELIEF OF NaOH INITIATED REACTION
REACTOR AND DISPOSAL CELL - TEMPERATURE Vs TIME

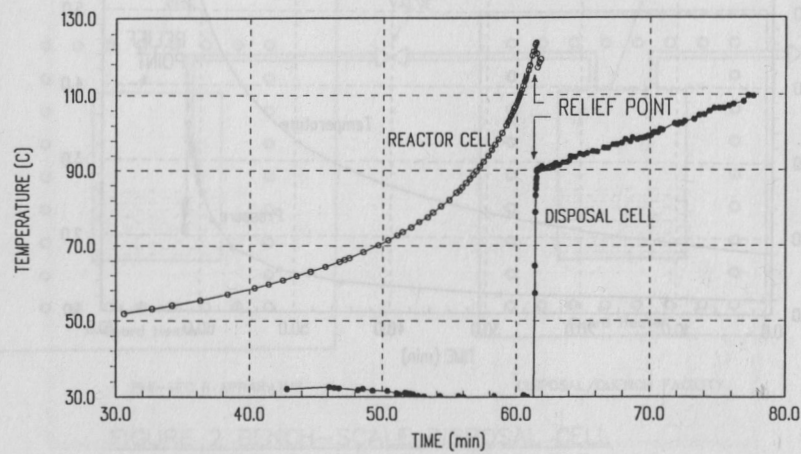


FIG 7 : RELIEF OF NaOH INITIATED REACTION
PRESSURE AND TEMPERATURE Vs TIME IN DISPOSAL CELL

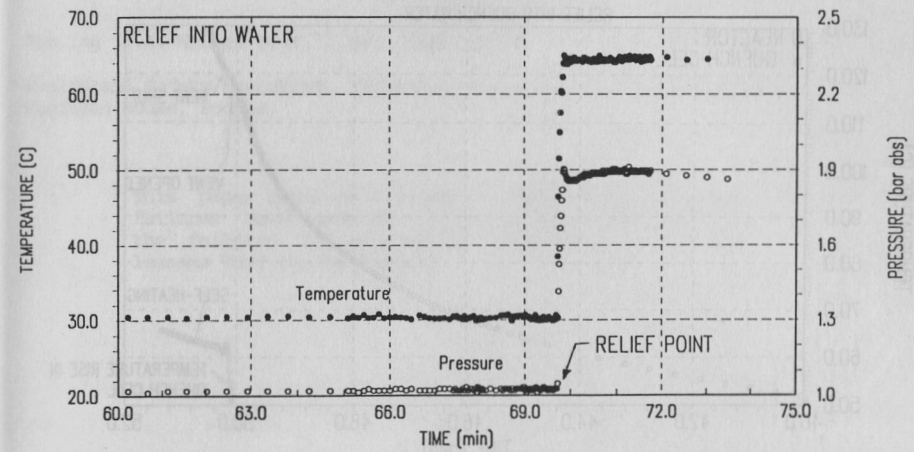


FIG 8 : METHANOL-ACETIC ANHYDRIDE RUNAWAY
PRESSURE & TEMPERATURE Vs TIME

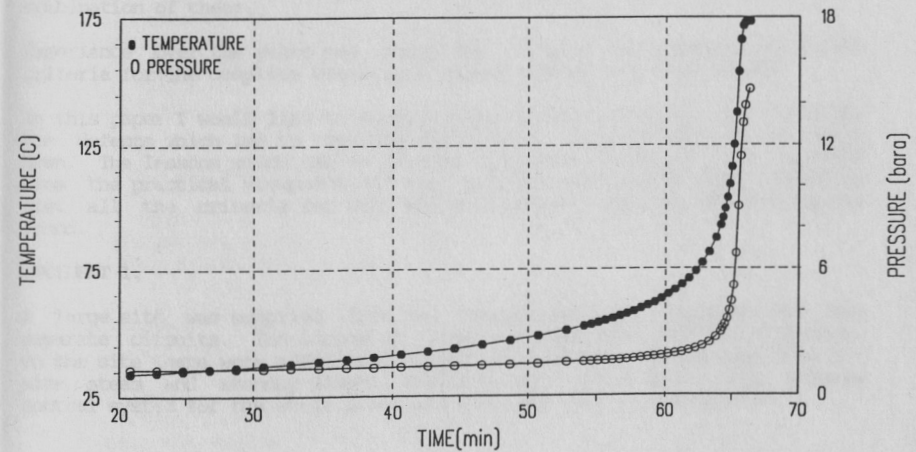
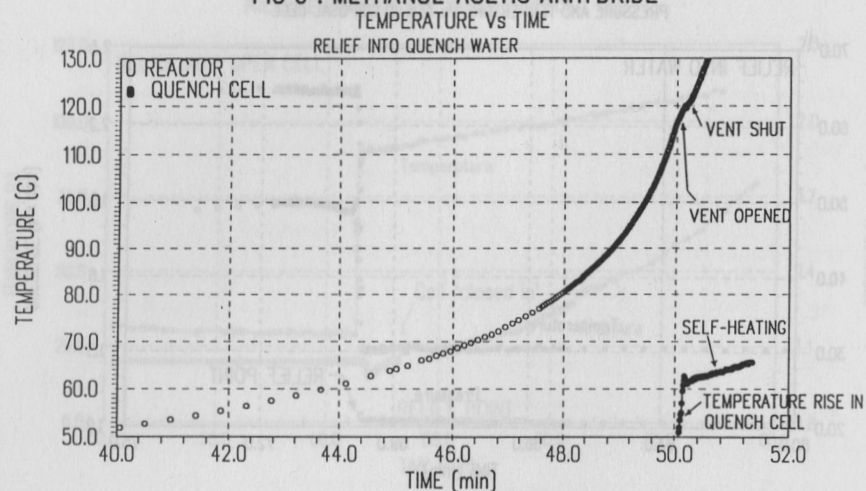


FIG 9 : METHANOL-ACETIC ANHYDRIDE



SECURITY OF ELECTRICAL SUPPLY SYSTEMS INCLUDING STANDBY SUPPLIES

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This paper examines a number of incidents where power failures have occurred. It examines the effects of the failures, the reasons for them and sets out the lessons that can be learned.

SECURITY OF ELECTRICAL SUPPLY SYSTEMS INCLUDING STANDBY SUPPLIES.

All process industries use electrical energy in many forms for the operation of instrumentation and control of their plants. The electrical systems used range from the very simple to the very complex and often incorporate standby supplies. These standby supplies may be diesel engine driven generators, self contained Uninterruptible Power Supplies, on-site steam and gas turbine powered generators or any combination of these.

Experience over the years has shown that in many installations the design criteria for the complete electrical supply system have been flawed.

In this paper I would like to examine some typical incidents and indicate the defects which led to failure and loss of control and/or plant shut-down. The lessons which can be learned from these incidents are valuable from the practical viewpoint, and are possibly more useful than trying to list all the criteria for each and every power supply system that may be found.

INCIDENT 1.

A large site was supplied from two independent Grid Supply Points via separate circuits. The routes of these circuits were totally different. On the site there were additional electrical supplies. These were from on-site steam and standby diesel engine driven generation. The process control system for the whole plant was provided with an alternative