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Workbook for chemical reactor relief system sizing

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Workbook for chemical reactor relief system sizing

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For a description of this research report, please read the Foreword on pages iii and iv.

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FOREWORD

The purpose of this Workbook is to give information on methods available for the sizing of emergency relief systems for exothermic runaway reactions in liquid-phase chemical reactors.

At present, there is no comprehensive guidance on this topic. However, it has been the subject of much research, particularly by the Design Institute for Emergency Relief Systems (DIERS) of the American Institute of Chemical Engineers (AIChE). As a result, the DIERS Project Manual[1] (a record of the DIERS research) and a considerable number of papers have been published. This Workbook summarises the main hand calculation methods (which do not need the use of a computer) available as a result of this work and their limits of applicability. A number of worked examples are given to help the reader understand their application. The experimental information required to size an emergency relief system properly is also discussed.

The Workbook is written mainly for chemical engineers or applied chemists with a good basic training in both chemical reaction kinetics and fluid flow. Experience of the development of appropriate physical properties from databases (or small-scale experiments if appropriate), for the reacting mixtures under consideration, is also needed. In addition, it is important that the assessment of chemical reaction hazards, including the selection of suitable test methods and the interpretation of kinetic data, is carried out by competent experienced personnel. Where it is not cost effective for companies to have their own "in house" reaction hazard assessment facilities, they may need to use a test house or consultancy[2,3].

The Workbook should also provide useful information for others who recognise that an emergency relief system may be required for their process and wish to ensure that the correct procedures have been followed in designing and maintaining it.

In addition to the hand calculation methods, there are also a number of computer models available for relief system sizing. The best known of these are referred to in the Workbook, but they are not dealt with in any detail. This is a highly specialised field and a potential user needs to discuss their application with the code supplier. A number of requirements for computer models are suggested.

Reaction hazard assessment, other than for the purposes of relief system sizing, is not dealt with. Information on this is given in reference 4. It is assumed that any process that has reached the relief system design stage has already undergone a preliminary assessment and exothermic runaway is foreseeable.

The Workbook does not deal with fire relief of vessels (except where external fire modifies the relief sizing for runaway exothermic reaction) or with the mechanical integrity of either the process vessels or relief system. Guidance on these is available elsewhere[5].

The technology of relief system sizing is continually evolving. The information contained in this document is based on the best currently available technology and may be subject to change.

Although every care has been taken to avoid errors, it would be impossible to guarantee that none had escaped detection. The authors would be grateful for any suggestions that readers may make concerning this. These may be sent to: Mr B Kemble, Gas & Chemical Process Safety Unit, Directorate of Science and Technology, HSE, Magdalen House, Trinity Rd., Bootle, Merseyside L20 3QZ, England.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

There are a number of means of achieving safe operation of chemical reactors. Usually the best option is to avoid the hazards completely, or at least minimise them, by inherently safer design. However, this may not be reasonably practicable and, to maintain a viable process, other safety measures will be required, either alone or in combination.

Where the hazard is an exothermic runaway reaction, there are a number of alternative measures that may be used either to prevent or control runaway. Information on the various options is in Annex 1. In the UK, one of the most commonly selected measures used to protect reactors from exothermic runaway is an emergency relief system. These have a number of advantages:

a) They are independent of the main control system.

b) They provide a relatively passive means of protection.

c) If all other systems fail, they may still provide adequate protection.

However, the design of emergency relief systems for exothermic runaway is complex. It requires a thorough understanding of the reaction during runaway, including any side-reactions or unintended reactions that may occur, and relief system sizing methodology. Information is required on:

a) The credible maloperations and system failures that might occur during reaction. *It is very important to assess the "worst case" for relief sizing from these credible maloperations and failures (see Chapter 3)*.

b) The kinetics of the reaction under runaway conditions.

c) Whether the reaction pressure is from vapour or gas (or both).

d) The flow regimes, both in the vessel and relief system, during relief.

e) The design and layout of the relief system.

Unless such information is used and applied properly in its design, then an emergency relief system may be wrongly sized and a false sense of security placed upon it.

At present, there is no comprehensive design guide on the sizing of emergency relief systems for exothermic runaway. However, over the last 20 years, a considerable amount of research has been carried out on the subject, particularly in the US by the Design Institute for Emergency Relief Systems (DIERS). This was a consortium of companies and other organisations (including HSE) that funded research costing $1.6 million between 1978 and 1985 and work has continued on a voluntary basis. There are also a number of research organisations and companies that are carrying out further research on the topic. As a result, the subject is better understood and a number of new relief system sizing methods are available. This has included both computer models and hand calculation methods (sizing formulae that can be solved with a pocket calculator or spreadsheet without the need for numerical modelling on a computer). These are described in a number of published papers, and in the DIERS Project Manual[1] (a record of the DIERS research project).

In most cases, a two-phase (vapour/ liquid or gas/ liquid) mixture is vented from a reactor emergency relief system. The relief system required for a two-phase mixture is very often larger (by, in some cases, several times the flow area) than for gas or vapour alone. It is therefore essential to take account of two-phase relief to size a relief system properly.

Certain historical sizing methods are invalid. For example, the so-called FIA method[2] (reviewed in reference 3), which was not originally intended for design purposes, has been withdrawn by its originators. As explained above, the assumption of gas or vapour-only relief, which is used in some methods, can be unsafe for relief sizing.

1.2 PURPOSE OF WORKBOOK

The main purpose of this Workbook is to summarise the principal hand calculation methods available (including those that were valid before DIERS) and their stated limits of applicability. Relief system sizing is by no means an easy subject, so a number of worked examples are given. The computer sizing methods are not dealt with in any detail although the main methods currently available are discussed in Annex 4. The computer models require a high degree of knowledge and expertise if they are to be applied properly and, if information on these is required, it is suggested that the suppliers of these models are consulted. Guidance on relief system design which emphasises the computer modelling approach has recently been produced in the US by the American Institute of Chemical Engineers' Center for Chemical Process Safety[4].

Unlike relief system sizing for non-reacting systems, a considerable amount of experimental information is normally required for the design of chemical reactor relief systems. It is necessary to assess all the credible maloperations and system failures that may occur on the process/ plant to determine the reaction runaway that requires the largest relief system. The Workbook also summarises the main steps necessary to do this.

Although there have been considerable advances in the technology over the last 20 years, it is still evolving. The information contained in this Workbook is a summary of the best available technology. Much work is still to be done and the design of relief systems for certain types of systems, e.g. viscous systems (>100 cP) and systems containing significant levels of solids, is still complex and is outside the scope of this document. Where emergency relief system design for any particular system is outside the scope of this Workbook, the reader is referred elsewhere, e.g. to specialist computer models.

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CHAPTER 2

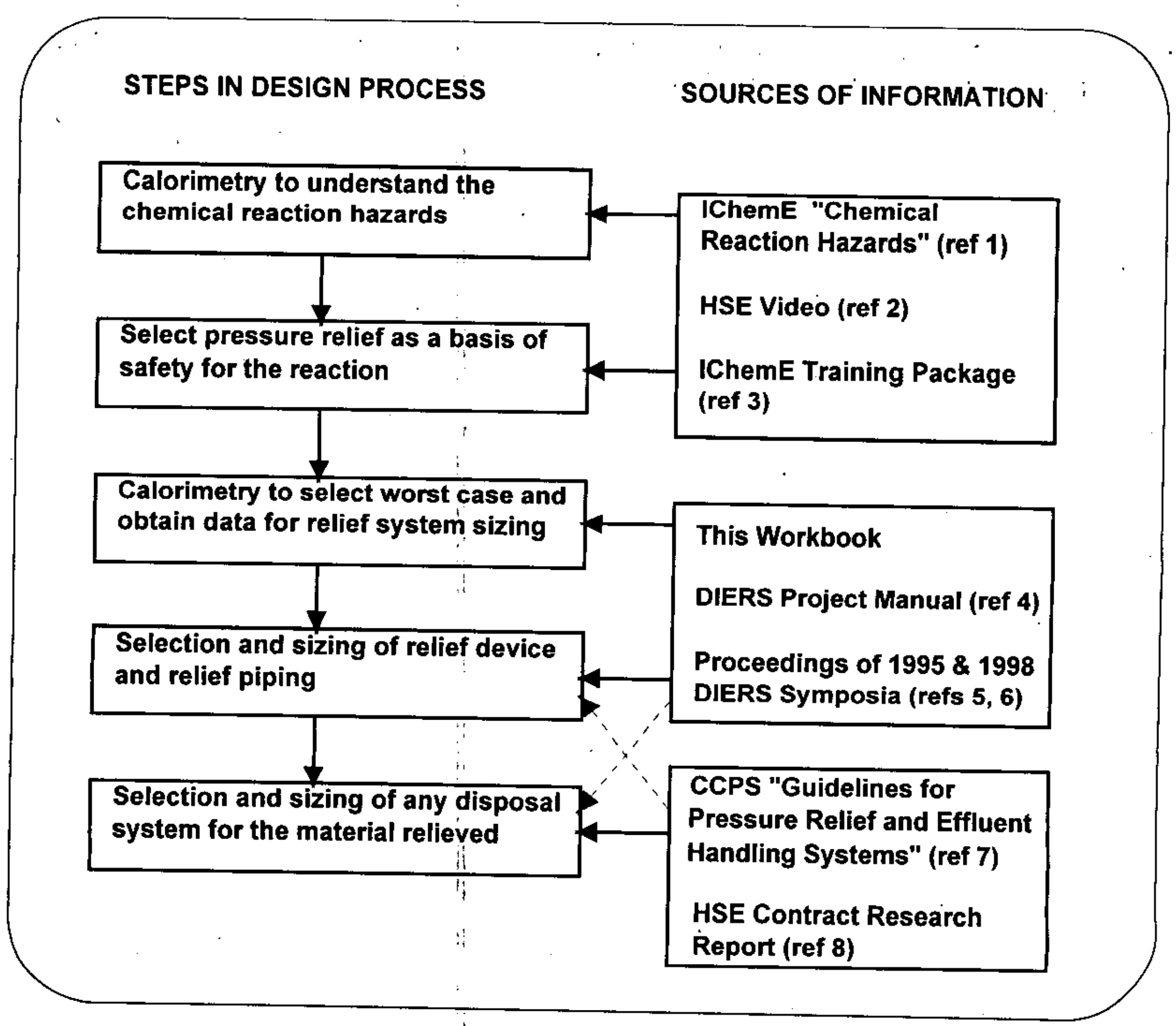
OVERVIEW

2.1 USE OF THE WORKBOOK DURING THE DESIGN PROCESS

The purpose of this chapter is to give an overview of this Workbook, from the point of view of its use during the design process of a pressure relief system for a chemical reactor.

Figure 2.1 illustrates the steps in the design of a pressure relief system, and indicates those steps which are covered by this Workbook.

Figure 2.1 STEPS IN THE DESIGN OF A PRESSURE RELIEF SYSTEM FOR A RUNAWAY CHEMICAL REACTION



The Workbook is intended to be self-sufficient for sizing calculations for the more straightforward applications. The emphasis of the Workbook is on the use of simple (yet adequate) equations, suitable for solving with a pocket calculator, rather than on more complex computer models.

The Workbook is concerned with "how to ?" more than with "why ?". Sizing methods are given together with conditions of applicability and some limited background information. Sources of information for theory, derivations of equations and some more unusual methods are referenced. Use is made of decision trees to guide the user to the appropriate part(s) of the Workbook. Worked examples are given for all the main methods.

2.2 STRUCTURE OF THE WORKBOOK

The structure of the Workbook is summarised by the flowchart in Figure 2.2 which indicates the paths to be taken through the Workbook when carrying out any particular relief system design.

The first two chapters of the Workbook contain background information. The design process begins with Chapter 3 which explains the process of determining the worst case relief scenario on which the relief system design is to be based. This process entails determining the credible combination of failures and maloperations which gives rise to the largest required relief size. The next stage in the design process, described in Chapter 4, is to determine the system type for relief sizing: vapour pressure, gassy or hybrid (a mixture of gas and vapour pressure). This system type leads into a particular set of methods for relief sizing (in Chapters 6, 7 or 8 respectively). Small-scale experiments are involved, which are described in Annex 2. Chapter 4 also deals with the determination of whether the relief flow will be:

a) two-phase vapour (or gas)/ liquid or gas/ vapour only; and

b) laminar rather than turbulent

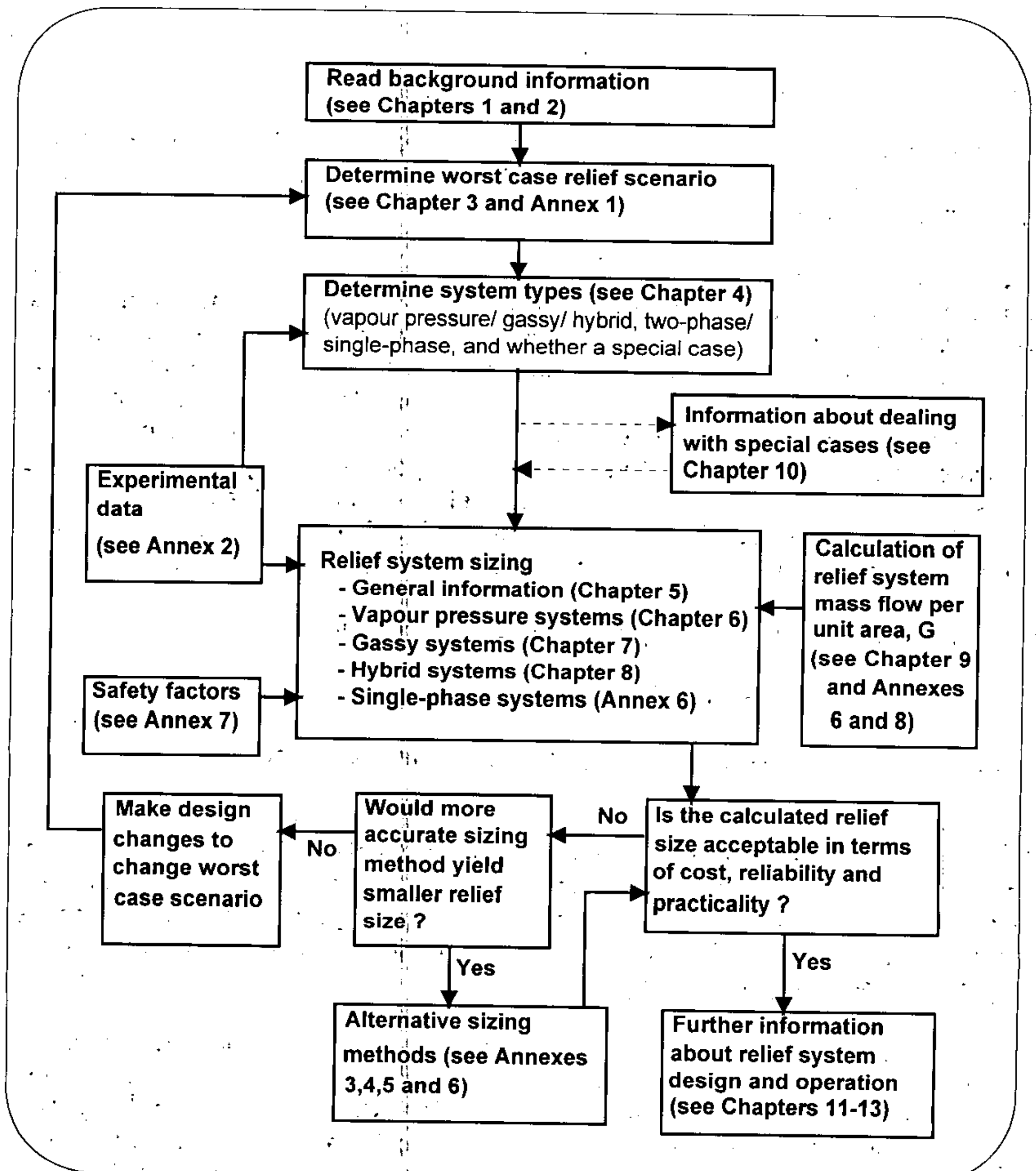
as these factors will affect the relief system sizing methods selected.

The relief sizing itself can then be carried out. Chapter 5 gives important background information about relief sizing. The following three chapters give sizing methods for each system type (vapour pressure, gassy and hybrid). In most cases, the simplest and most usual methods are given first, followed by suggested alternative methods (detailed in Annexes) should the initial methods be inapplicable or likely to oversize due to their underlying assumptions.

Most of the relief sizing equations given in Chapters 6-8 yield the two-phase required relief rate, W. The two-phase mass flow capacity per unit area, G, is then needed in order to obtain the required relief area. Chapter 9 contains important background information about two-phase flow, and calculation methods for G. Some system types are special cases involving highly viscous (laminar) flow, solids and/or multiple liquid phases. In these cases, Chapter 10, rather than Chapter 9, should be read in conjunction with Chapters 6-8.

Chapters 11-13 cover the selection and sizing of downstream disposal systems, reaction forces which require piping and vessel supports, maintenance, documentation and change management. Additional material is given in Annexes 1-8 and is referenced from the text as required. This includes consideration of any safety factor to be applied to the calculated relief size.

Figure 2.2 FLOW CHART FOR USE OF THE WORKBOOK



The design of a relief system often involves iteration and recycle. The flow chart in Figure 2.2 shows that possible recycle in the design process may involve changing the assumptions about the worst case relief scenario or changing the sizing method used.

2.3 LAYOUT OF THE WORKBOOK

Sections and sub-sections are numbered using a decimal system. Thus, 7.4.1 is the first sub-section of section 4 of Chapter 7; A3.5.2 is the second sub-section of section 5 of Annex 3. Section numbers, rather than page numbers, are used to cross-reference material in other parts of the Workbook. Figures and Tables are numbered consecutively within each chapter, e.g. Figure A2.1 is the first figure in Annex 2. Equations are also numbered consecutively within each Chapter, with the equation number appearing in brackets at the end of the equation.

Each Chapter or Annex has its own list of references at its end. A glossary, a nomenclature list and an index for the entire Workbook appear in Annexes 9, 10 and 11, respectively.

REFERENCES FOR CHAPTER 2

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CHAPTER 3

DETERMINING THE WORST CASE

3.1 INTRODUCTION

The "worst case" for emergency relief system sizing is the scenario in which a credible combination of equipment failures and process maloperations occurs and gives rise to the largest calculated relief system compared with other credible scenarios. This worst case can therefore be safely used as the design basis for the emergency relief system. It is particularly important to understand that the worst case for vent design purposes will depend upon how each maloperation influences the system during relief, and this needs to be assessed separately for each case.

The recommended procedures to determine the worst case include the following:

a) Consider the most appropriate basis of safety for the reactor (see 3.2 and Annex 1). (This may lead to the conclusion that pressure relief is inappropriate.)

b) If pressure relief is being considered, list the credible maloperations, including system failures, that could lead to exothermic runaway and vessel over-pressurisation (see 3.3 and reference 1).

c) Determine how the system pressure is generated (vapour pressure, gassy or hybrid system - see 3.4). This will determine the type of kinetic data which needs to be obtained for relief system sizing.

d) Select the worst case or a small number of possible candidate worst cases (see 3.5). This is likely to be done using screening techniques.

e) Final selection of the worst case from a small number of options (see 3.5.2). This is likely to require similar calorimetry and calculations to those needed for relief system sizing. In order to compare possible options for the worst case, the sizing calculations can be done on the basis of no relief line friction.

f) Size the relief system based on the measured kinetic data for the worst case and using actual dimensions of the relief system piping.

g) If the calculated relief system size is too large, either:

   i) reconsider the basis of safety (step a), and/or

ii) provide reliable means to prevent the worst case maloperations and system failures (step b) in order to reduce the required relief system size.

The procedure to determine both the basis of safety for the reactor (see Annex 1) and the worst case scenario for that basis of safety is iterative. The same screening tests which help determine the worst case for pressure relief sizing may lead to the conclusion that pressure relief is not the best basis of safety. The results of screening tests may also indicate that it is worthwhile to seek a more inherently safe solution by designing out the possibility of certain maloperations or system failures (for example, if the screening indicates that a very large relief system would be required).

A flow chart illustrating the above iterative process is given as Figure 3.1.

3.2 BASIS OF SAFETY

The need for an emergency relief system should be considered as part of an overall basis of safety. Before deciding that an emergency relief system is necessary, the process designer should have considered whether or not it is possible to prevent vessel over-pressurisation by design. Alternatively, other methods of reactor protection, such as quenching, may be appropriate. Information on methods of preventing runaway (both inherently safe methods and active methods) and protection from runaway is given in Annex 1 and references 1-3.

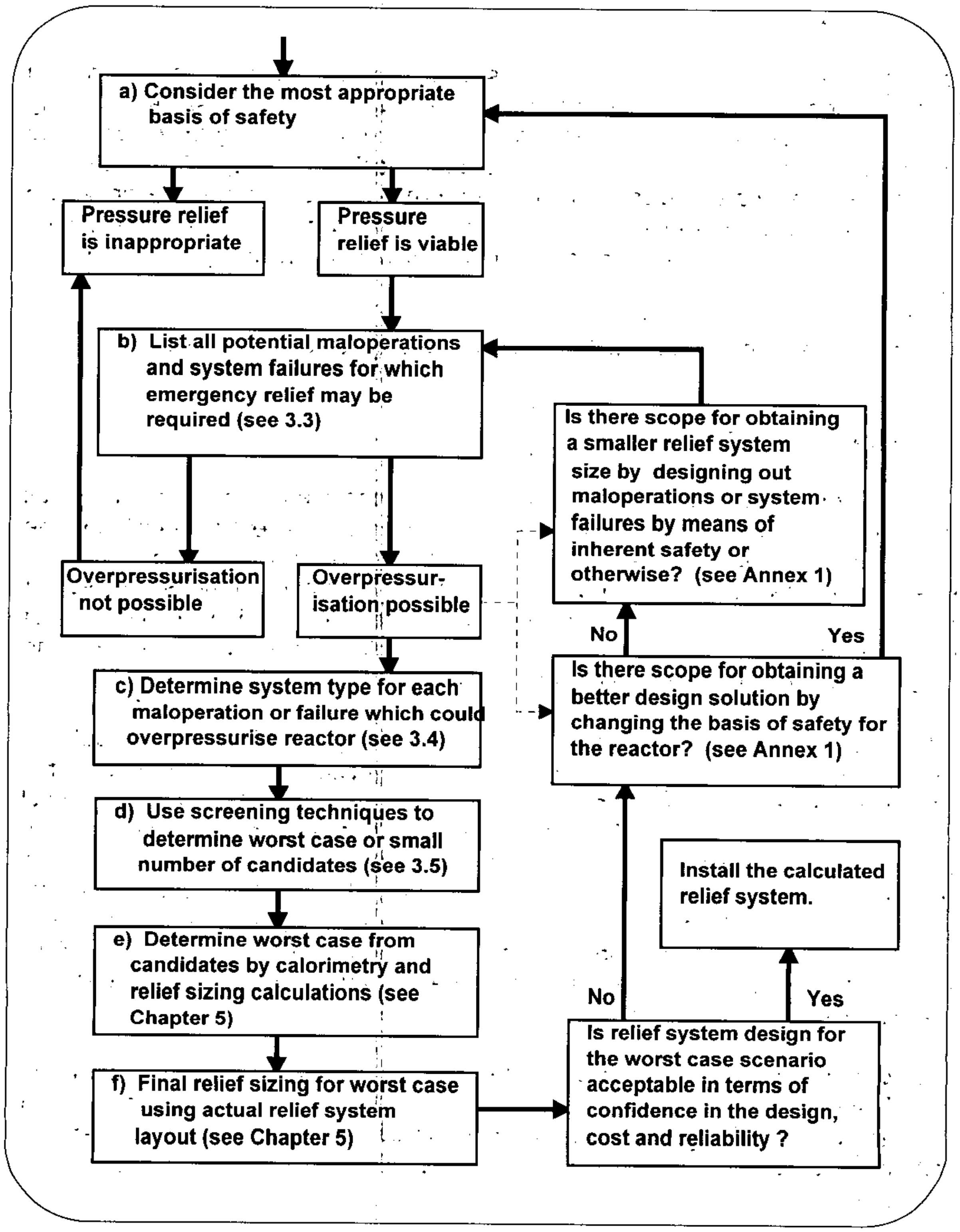
As the reaction hazard assessment proceeds and more information about the system becomes known, it may be decided that pressure relief is no longer the best option. For example, at stage (f) above it may become clear that, for a small increase in design strength, the reactor may be designed to contain the peak reaction pressure.. Such containment may be a better option, particularly where hazardous materials are involved, as it eliminates the need for costly disposal systems. It also avoids the lengthy experimental work that may be needed for relief system design. However, care needs to be taken that no other reactions, especially decompositions which produce permanent gas, occur at the peak temperature corresponding to the peak pressure.

It should be noted that the worst case scenario may be different depending on the basis of safety being considered. For example, the worst case for emergency relief sizing may be that giving rise to the highest rate of heat generation. However, the worst case for containment will be that giving the highest final pressure and temperature.

3.3 CREDIBLE RELIEF SCENARIOS

If the decision has been made to install an emergency relief system, then further information will be required about the reacting system, both under normal and

Figure 3.1 FLOW CHART ILLUSTRATING THE SELECTION OF THE WORST CASE DESIGN CONDITIONS FOR A RELIEF SYSTEM



abnormal conditions, so that it can be designed for all the credible maloperations (including system failures) that can occur on the plant. The information that is obtained will need to reflect accurately what could happen on the full-scale plant and a high degree of care needs to be taken in obtaining it. The first step is to define the events or credible combinations of events that could give rise to a need for pressure relief.

3.3.1 Consideration of Process Maloperations and System Failures

The full range of process maloperations, including system failures, that might lead to process runaway will first have to be considered by a systematic evaluation of the plant and process concerned[4]. These may, for example, be due to human error, hardware failure, or due to failure of a computerised sequence controller. To assess the likely/ credible maloperations accurately, it is recommended that personnel who will be operating the plant are involved in the hazard assessment.

A list of typical maloperations is given in Figure 3.2. However, it should be noted that these will be specific to the process and plant concerned and *this list should not be regarded as comprehensive.*

Figure 3.2 TYPICAL MALOPERATIONS

Possible maloperations include:

- Incorrect charging sequence
- Cooling failure
- Agitator failure or restart of agitator after failure
- Contamination of reactants
- Additions too quickly
- Delayed addition
- Temperature too low/ high
- Incorrect reaction
- Concentration
- Removal of volatile diluents
- Failure of heating to turn off

3.3.2 Credible scenarios

It may not be credible that multiple simultaneous failures and maloperations occur. In considering what is credible, the following points may be useful:

a) Certain failures may occur and not be noticed or rectified for a considerable period of time. This can include both hardware failures, especially of trip systems, and software failures such as failure to properly follow procedures. If such a failure or failures could occur then it is credible to consider them together with a sudden failure or maloperation which would initiate a runaway.

b) In a well maintained and managed process plant, two simultaneous sudden failures that would each prevent normal operation and/or be quickly identified and rectified are may not be credible (except in the case of (c) below).

c) Certain failures or maloperations will either directly cause other failures or increase their likelihood. Such failures are often described as "common cause" or "common mode". For example, if a reacting fluid is capable of causing blockages, then it could simultaneously block all the pressure measurement points and build up on thermocouples, thereby interfering with temperature measurement; external fire could cause a thermal runaway; power failure could cause cooling failure and valves to open or close.

It will then be necessary to check whether or not the credible maloperations can lead to exothermic runaway. Information on this is given in reference 1. Where it is shown that runaway can occur, and it is decided that emergency pressure relief may be used as part of the basis of safety, then it will be necessary to carry out further work to identify the worst case for relief system sizing.

3.4 KINETIC DATA REQUIRED FOR DETERMINING THE WORST CASE

3.4.1 Introduction

The worst case scenario is that which gives rise to the largest required relief size. Thus, the kinetic data required to determine the worst case is essentially the same as that required for relief system sizing. However, the determination of the worst case is a screening process rather than requiring detailed relief sizing for each scenario. Therefore the kinetic data required for the simplest sizing methods are sufficient.

3.4.2 System types

In order to design a relief system, it is necessary to obtain specific kinetic data. The data required, and hence the worst case, depends on how the system pressure is generated. For the purposes of relief system sizing, there are three system types, these are:

a) Vapour pressure systems: The pressure generated by a runaway reaction is entirely due to the vapour pressure of the reacting mixture, which rises as the temperature of the mixture increases during a thermal runaway.

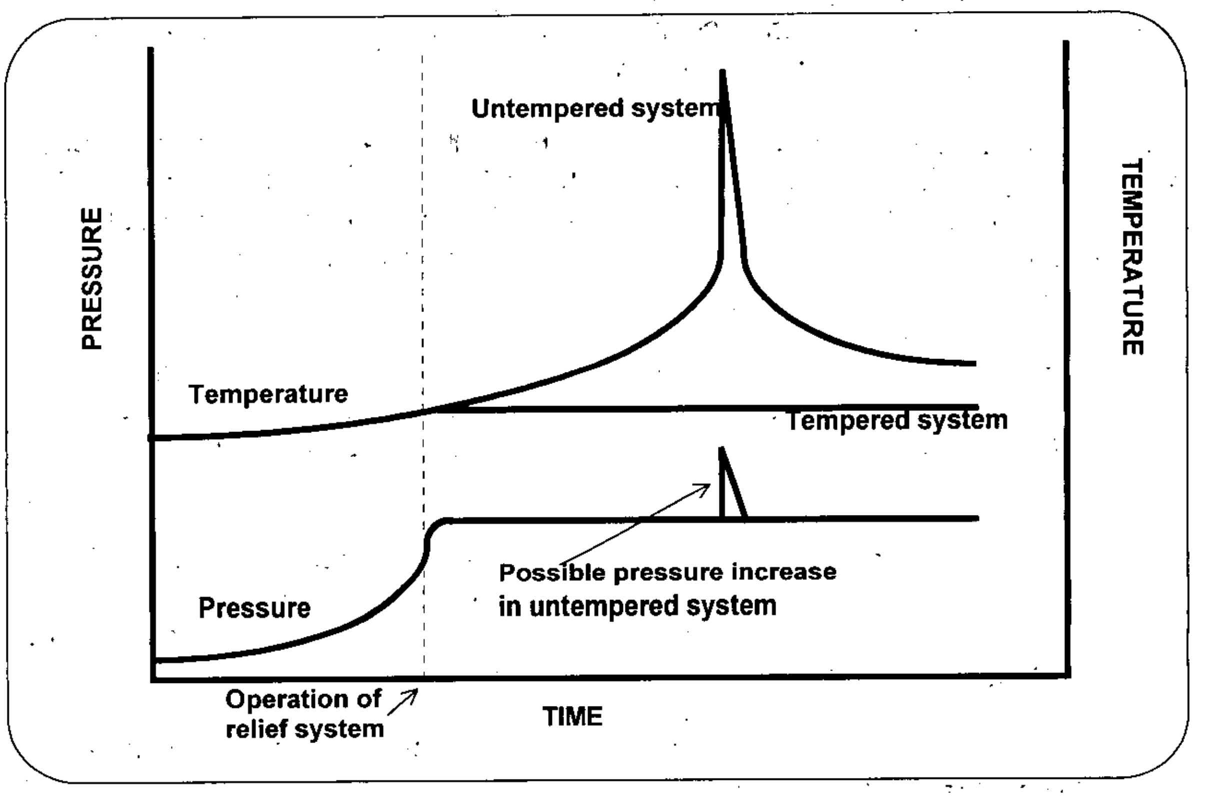
b) Gassy systems: The pressure generated by a runaway reaction is almost entirely due to a permanent gas which is evolved by the chemical reaction.

c) Hybrid systems: The pressure is due to both evolution of a permanent gas and increasing vapour pressure with increasing temperature.

For vapour pressure systems, the emergency relief system should be designed so that the action of the pressure relief system removes vapour (and therefore latent heat) at a rate fast enough to hold the temperature, and therefore the pressure, constant. This is referred to as a "tempered" reaction system (see Figure 3.3). In most cases, the rate of reaction does not then increase beyond this point. However, it is worth noting that, in some cases, the reaction rate may continue to rise at constant temperature and pressure if:

a) the change in composition, due to the chemical reaction and to the preferential vaporisation of the more volatile components, raises the boiling point of the reacting mixture; or

Figure 3.3 BEHAVIOUR OF TEMPERED AND UNTEMPERED SYSTEMS DURING RELIEF



b) some other parameter than temperature can influence reaction rate, e.g. pH, autocatalysis.

In such cases, the reaction can often still be treated as tempered for relief sizing purposes but a higher reaction rate should be used for relief sizing (see 6.3.1).

Gassy systems are "untempered". Removal of gas from the relief system will not stop the temperature from rising and the volumetric rate of gas generation will continue to increase. The relief system should be designed to cope with the maximum rate of gas generation that can occur before the vessel empties. For untempered systems, it is important to check (by testing) whether or not, as the temperature rises, secondary reactions or decompositions occur (see also Figure 3.3). These can have a much greater rate of gas generation than the initial runaway reaction and the relief system design should take account of this.

Hybrid systems may be either tempered or untempered. Generally, untempered systems require much larger relief systems than tempered systems. It is often important that advantage is taken of this in the design of relief systems for tempered hybrids.

Information on the determination of system type is given in Chapter 4 and Annex 2.

3.4.3 Kinetic information required to determine the worst case

Figure 3.3 shows the typical behaviour of both tempered and untempered systems during relief, with a properly designed relief system. The information that is required for the purposes of relief system design will depend upon how the system pressure is generated and whether or not the system is tempered.

To design a relief system, it is necessary to know how the system would behave under runaway conditions (i.e. between the relief opening pressure and the maximum accumulated pressure of the vessel). The appropriate temperatures at these pressures are different depending on whether or not the system is tempered or untempered.

For vapour pressure systems this will depend on the rate of temperature rise. Since the reaction will be tempered, the rate which is of interest is that at the average temperature between the relief pressure and the maximum accumulated pressure.

For gassy systems, this will depend on the rate of pressure rise in a closed system (rate of gas generation). Since gassy systems are untempered, the rate of interest is the maximum rate. This is likely to be at close to the maximum temperature reached by the runaway.

For hybrid systems this will be a combination of both the rate of temperature and pressure rise. Whether these should be measured at the relief pressure or the maximum temperature depends on whether the system is tempered or untempered.

Further information is given in Chapters 6 to 8.

The worst case will normally be the maloperation that results in the highest rate of temperature and/or pressure rise over the relief range (dependent on whether the system is tempered or untempered). However, this assumes that other parameters used in the relief sizing calculations remain constant, e.g. reactor fill ratio, mass of reacting species, physical properties. Where any of the other parameters used in the calculations are significantly affected by the maloperation under consideration, then this will also have to be taken into account in selecting the worst case. In such cases, it may be necessary to roughly calculate the relief size.

3.5 SELECTION OF WORST CASE SCENARIOS BY SCREENING

3.5.1 General

At this stage, a number of credible maloperations will have been defined that can lead to vessel over-pressurisation. In order to cope with all the credible runaway scenarios, the relief system will need to be sized for the "worst case runaway" reaction that can occur, and this is normally the maloperation that will give rise to the highest rate of temperature and/or pressure rise over the relief range.

Determination of the worst case is by no means straightforward. It is important that selection is on the basis of rate of reaction rather than heat of reaction, even though heat of reaction is more easily measured in a screening apparatus.

Ideally, the rate of temperature or pressure rise would be measured in adiabatic calorimeters specifically designed for relief system sizing (see Annex 2). These generally give a good indication of conditions in a full-scale reactor during runaway as the heat losses from the sample are minimised. However, the use of such calorimeters to obtain data for all possible relief scenarios may be time-consuming and costly.

Alternatively, with a knowledge of the reaction kinetics, it may be possible to rule out certain scenarios as being unlikely to produce the worst case. However, the reaction kinetics used to do this must be based on the reaction that actually occurs under runaway, rather than the reaction that is theoretically expected. A degree of testing of the reaction under runaway is usually needed and, for the information to be sufficiently reliable, this should normally have been obtained using a purpose built vent sizing calorimeter (see Annex 2). It is essential that personnel who are experienced in carrying out these tests are involved in the assessment.

3.5.2 Non-adiabatic screening tests

Non-adiabatic screening tests such as Carius tube[1] and the Accelerating Rate Calorimeter[1] (ARC™), corrected for sample heat losses due to thermal inertia, can also be used for screening. If it is known that the reaction is a vapour pressure system, DSC[1] may be used.

Most screening tests are likely to lump all reactions that generate gas together. Tempered hybrid systems will not be distinguished but these will require a smaller relief area than a gassy system with the same gas generation rate. If the worst case is subsequently found to be a tempered hybrid reaction, rather than a gassy system, then some reiteration to check that it is still the worst case may be required.

If all the identified relief scenarios give rise to the same system type, then the worst case is likely to be that which gives the highest rate of reaction, at the appropriate temperatures, in the screening test, as follows:

a) For vapour pressure systems, for screening purposes, the worst case can be approximated to that which gives the maximum rate of temperature rise at the temperature corresponding to the relief pressure.

b) For gassy systems, the worst case can be approximated to that which gives the highest maximum rate of pressure rise. This will usually be at approximately the maximum temperature reached by the runaway.

However, it must be recognised that these maximum rates will be underestimates due to the heat losses from the sample in the tests. Careful interpretation is needed when using such non-adiabatic screening tests to find the worst case, and this is best done by skilled and experienced analysts. In addition, for gas-generating systems, it may be difficult to contain the peak pressure using a screening test such as the Carius tube. The use of an adiabatic screening test (see 3.5.3 below) may therefore be preferred.

Non-adiabatic screening tests can be used to narrow down the range of relief scenarios which may be the worst case, but in many cases two or three possibilities may still remain.

3.5.3 Adiabatic screening tests

The RSST™ calorimeter (see Annex 2) is a pseudo-adiabatic, low thermal inertia calorimeter, intended for screening purposes. It can identify the system type and measure adiabatic rate of temperature rise and rate of gas generation by the reacting mixture. It is therefore well-suited to the task of selecting the overall worst case scenario from a small number of candidates. Alternatively, a calorimeter designed to obtain relief system sizing data may be used for this purpose (see Annex 2).

In each case, relief sizing calculations need to be performed using the calorimetric data to determine the scenario requiring the largest relief area. Fauske et al.'s nomographs[5] can be used for this purpose. Versions of the nomographs, specific to the RSST™ calorimeter are included in the RSST™ documentation. These nomographs and their underlying assumptions are discussed in A5.16. Alternatively, simple calculation methods for relief sizing, e.g. those given in A5.3 and A5.15, can be used for this purpose.

If the nomographs are used to distinguish between two candidate worst case scenarios, care should be taken that the decision is not invalidated by the relief design calculations. For example, the nomographs could suggest that the worst case is a gassy reaction because the nomograph for gassy reactions is based on assumptions which are sometimes very conservative. If the relief sizing calculations were then carried out using a dynamic computer simulation and yielded a much smaller relief size than that given by the nomograph, then the decision about which relief scenario is the worst case should be re-evaluated.

3.6 MULTI-PURPOSE VESSELS

For multi-purpose vessels there will be a much larger number of possible relief scenarios. The worst case can be found using the methods above, but the process may be more time-consuming because many more possible scenarios are likely to be identified. Sometimes different relief systems may be specified for the different reactions that are carried out in a reactor, and the bursting disc must be changed to the correct one at the beginning of a campaign. A robust procedure is clearly needed to ensure that this occurs.

Whenever a new reaction is introduced into a multi-purpose reactor, an assessment of the adequacy of the relief system needs to take place. If necessary, the relief system will need to be modified before the new reaction begins to be used. At the same time, the adequacy of the new relief system for all other reactions that are performed in the reactor will need to be checked, especially if the modification involves an increase in relief pressure due to a higher operating pressure for the new reaction.

It may be possible to minimise the time spent on relief system assessment and design if the basis of safety for a multi-purpose reactor can be changed to prevention rather than emergency pressure relief. For example, if it can be arranged for all the reactions to operate in semi-batch mode with no significant reactant accumulation, then the use of a trip system of sufficient integrity may provide a suitable basis of safety. (This may not always be possible.)

3.7 EXAMPLE

This is a simplified idealised example to illustrate some of the points made in this Chapter.

3.7.1 Description of the problem

A semi-batch reaction is designed to involve the following steps:

1. Charge 2000 kg of inert solvent to the reactor with the agitator running and heating on to raise the temperature to 80°C.
2. Charge 150 g of catalyst in 2 litres of solvent.
3. When the temperature has reached 80°C, and with the agitator running, gradually add the reactant at a rate of 1000 kg/h. An exothermic polymerisation reaction occurs and the control system turns off the heating and supplies cooling to maintain the temperature at 80°C.
4. Stop the addition of reactant when 1500 kg have been added. Continue the polymerisation, controlling the temperature at 80°C for a further 30 minutes. Over this time, the control system will change from cooling to heating mode as the reaction nears completion.
5. Discharge the product by gravity to the next stage of the process.
6. Wash the reactor using high pressure water jets.

3.7.2 Hazard analysis

A hazard analysis has identified the following failures and maloperations which may give rise to a runaway reaction:

a) Omission of the solvent.

b) Omission of catalyst followed by its addition at the end of step 4.

c) Overcharging of catalyst.

d) Heating/ control system failure such that step 3 (and therefore step 4) occurs when the temperature is significantly below 80°C.

e) Heating/ control system failure such that the heating remains on in steps 3 and 4 and the cooling system fails to come on during step 3..

f) Failure to start the agitator until the end of step 4.

g) Failure to stop addition of reactant in step 4 after 1500 kg have been added.

h) Addition of reactant faster than 1000 kg/h in step 3.

j) Wash-water remaining in reactor at the start of the next batch.

Heat flow calorimetry indicated that failure of the heater control to switch off and of cooling water to switch on (case (e)) was not a problem, since the steam heating is unable to exceed 100°C and, for this semi-batch reaction, the total temperature increase only reduces further any reactant accumulation. This means that cases (b), (f) and (d) are all worse than case (e).

Case (h) was subsequently removed by installation of a site-registered flow restrictor as a back-up to the flow controller.

3.7.3 Screening

From the above, the following mixtures were selected for screening using the Carius tube apparatus[1]:

i) Mixture corresponding to recipe proportions of solvent, reactant and catalyst (all-in batch). This would be the result of cases (b) and (f). For case (d), it would correspond to no initial reaction due to the low temperature followed by runaway (perhaps due to reinstatement of heating) once all the reactant had been added. Runaway of this mixture may occur if either:

- the rate of heat generation by the reaction exceeds the capacity of the cooling system; or

- simultaneous cooling failure occurs.

Although the Carius tube test is not adiabatic, cooling is reduced substantially by the heating oven so that it roughly simulates the effect of simultaneous cooling failure. It does not take into account the heat losses if cooling were maintained. Further testing, such as heat flow calorimetry[1], would be needed to determine whether or not a runaway would occur without simultaneous cooling failure.

ii) Mixture corresponding to normal quantities of solvent and reactant with twice the normal quantity of catalyst. The test corresponds to overcharging of catalyst (case (c)) simultaneously with events which would lead to an "all-in" batch situation (i.e. all reactants charged to the reactor at the same time). Again, consideration could be given to whether this would be credible. Many versions of the Carius tube cannot handle gradual addition of reagents and so cannot be used to test whether increased catalyst concentration together with the normal addition rate of the reactant would lead to a runaway. Other tests which can simulate the reactant addition could be used to determine this.

iii) Mixture corresponding to the normal quantities of reactant and catalyst but with no solvent (case (a)). The Carius tube can only test an all-in mixture. However, this may be what occurs if effective agitation (to mix in the catalyst) does not occur until late in the reactant addition when the level rises above the agitator.

iv) mixture corresponding to the normal quantities of solvent and catalyst with twice the normal amount of reactant. This is a subset of case (g).

v) mixture corresponding to normal quantities of solvent catalyst and reactant, plus a quantity of water. This is to simulate case (j).

Results from the Carius tube tests were as shown in Table 3.1

Table 3.1 Carius tube test results for example problem

Case	Maximum temperature (°C)	Maximum pressure (bar)	Maximum rate of pressure rise (bar/s)	Maximum rate of temperature rise (°C/s)	Rate of temperature rise at relief pressure (°C/s)
i	220	5	0.1	3.6	0.7
ii	223	5.2	0.25	5.7	1.3
iii	330	15+	3+	2.4+	N/A
iv	250	7	0.4	6.5	0.75
v	218	5.5	0.1	3.5	0.7

Analysis of the pressure versus temperature data for the tests (see Annex 2) indicated that case (iii) generated permanent gas but that the other cases were vapour pressure systems. For a vapour pressure system, it is the rate of temperature rise at the relief pressure which determines the relief system size. The relief pressure of 3 bara corresponds to a temperature of approximately 100 °C for cases (i), (ii) and (v); and to approximately 80°C for case (iv). It can be seen from Table 3.1 that case (ii) gives the highest rate of temperature rise at that temperature and is therefore the worst of the vapour pressure systems.

In order to decide whether case (ii) or case (iii), in which permanent gas was produced, is the worst case, some kind of sizing calculation is required. It must be emphasised that the use of non-adiabatic Carius tube data in a sizing calculation will not give the correct relief system size. However, it may distinguish the worst-case if one scenario gives a much larger size than the other.

Fauske's method for vapour pressure systems (see A5.3) and the sizing method for gassy systems (see Chapter 7) have been used to do a very approximate relief sizing. Alternatively for screening purposes, nomographs[5] could be used.

For case (ii), Fauske's method (assuming homogeneous venting) is:

$$A_{\text{approx}} = \frac{1}{2}\frac{m_R (dT/dt)_R}{F\,\Delta P}\sqrt{\frac{C_{fR}}{T_R}} \qquad \text{(A5.5)}$$

m_R is the mass in the reactor, 3500 kg.

$(dT/dt)_R$ is the rate of temperature rise at the relief pressure, i.e. 1.3 °C/s (see Table 3.1).

F is a friction correction factor. For screening purposes, this has been taken as 1 (no friction) for comparison with a relief area for case (iii) which also ignores friction.

ΔP is the overpressure allowed. This has been taken to be 30% of the relief pressure of 3 bara, i.e. 0.3 x 3 = 0.9 bara = 0.9×10^5 N/m^2.

C_{fR} is the liquid specific heat capacity and a typical value for organics of 2500 J/kgK has been used. T_R is the relief temperature, which is 100°C or 373 K. Thus:

$$A_{\text{approx}} = \frac{1}{2}\frac{3500\text{x}1.3}{1\text{x}0.9\text{x}10^5}\sqrt{\frac{2500}{373}} = 0.06 \quad \text{m}^2.$$

For case (iii) the gassy system method from Chapter 7 has been used:

$$W_{\text{approx}} = Q_{G\max}\frac{m_R}{V} \tag{7.1}$$

The volumetric gas generation rate, $Q_{G\max}$, is calculated as 9.8 m^3/s (see A2.5), given the maximum rates of temperature and pressure rise from Table 3.1 before seal failure.

The reactor volume, V, is 5.5 m^3. The mass in the reactor, m_R, for this case is 1500 kg.

Thus $W_{\text{approx}} = 9.8\text{x}\frac{1500}{5.5} = 2673 \quad \text{kg/s}$

The required flow area is obtained from equation (5.1):

$$A = \frac{W}{G}$$

The two-phase mass relief capacity per unit area, G, ignoring friction, can be estimated using Tangren et al.'s method (see 9.4.3). This requires the void fraction in the reactor, α_0, which is approximately 0.6 for this case. Tangren's method is:

$$G = \sqrt{\frac{P}{V}}\frac{\left[\frac{2}{\alpha_0}\left(\frac{1-\alpha_0}{\alpha_0}(1-\eta)-\ln\eta\right)\right]^{0.5}}{\frac{1}{\eta}+\frac{1-\alpha_0}{\alpha_0}} \tag{9.8}$$

where $\eta = \left[2.016 + \left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714}$ (9.5)

provided flow is choked For α_0 0 6

$$\eta = \left[2.016 + \left(\frac{1-0.6}{2\text{x}0.6}\right)^{0.7}\right]^{-0.714} = 0.523$$

If the maximum pressure, P, is taken as 3 bara plus 30%, i.e. 3.9 bara then the critical pressure is 0.523 x 3.9 = 2.04 bara which exceeds atmospheric pressure. Flow is therefore confirmed as being choked. The two-phase specific volume, v, is the reactor volume divided by the mass in the reactor, i.e. 5.5/1500 = $3.67\text{x}10^{-3}$.

$$G = \sqrt{\frac{3.9\text{x}10^5}{3.67\text{x}10^{-3}}}\ \frac{\left[\frac{2}{0.6}\left(\frac{1-0.6}{0.6}(1-0.523)-\ln(0.523)\right)\right]^{0.5}}{\frac{1}{0.523}+\frac{1-0.6}{0.6}} = 7174 \quad \text{kg/m}^2\text{s}$$

The relief area can then be calculated:

$$A_{\text{approx}} = \frac{2673}{7174} = 0.373 \quad \text{m}^2$$

This is an underestimate because of the seal failure in the test, but is over 5 times larger than that obtained for case (ii). It can therefore be concluded that case (iii) is the worst case.

The use of the sizing method above for gassy systems assumes that case (iii) is not a tempered hybrid. If, during detailed relief sizing, case (iii) does turn out to be a tempered hybrid system, and the vent size is significantly smaller, then the worst case would need to be reassessed, by carrying out detailed relief sizing for both cases (ii) and (iii).

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CHAPTER 4

CLASSIFICATION OF RELIEF SYSTEMS

4.1 INTRODUCTION

The method employed for pressure relief system sizing will depend on the classification of the reacting system according to:

a) the reaction chemistry and system physical properties, in particular whether pressure is generated mainly as vapour or gas (see 4.2);

b) the hydrodynamics (level swell) in the reaction vessel, which determines the type of flow in the pressure relief system;

c) the viscosity of the system and whether the vent flow would be expected to be turbulent or laminar.

A starting point for relief sizing is therefore to determine the system types according to each of the above classifications. The appropriate Chapter (6, 7 or 8) can then be consulted for relief system sizing.

4.2 CLASSIFICATION OF SYSTEM TYPE FOR RELIEF SIZING

4.2.1 Types of system

For the purposes of relief system design, there are three main types of system dependent on the reaction being studied. These are:

(a) Vapour pressure systems: The pressure generated by a runaway reaction is entirely due to the vapour pressure of the reacting mixture, which rises as the temperature of the mixture increases during a thermal runaway.

(b) Gassy systems: The pressure generated by a runaway reaction is entirely due to a permanent gas which is evolved by the chemical reaction.

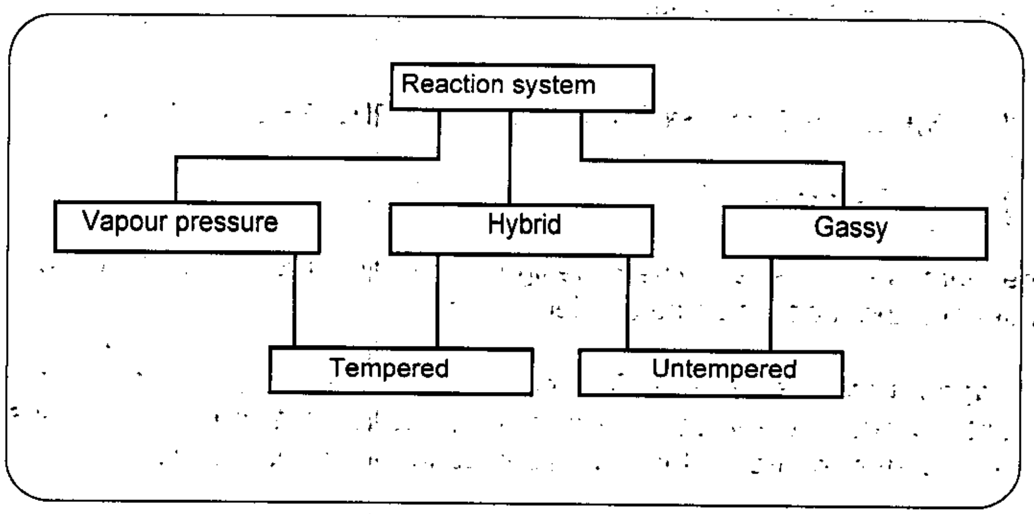
(c) Hybrid systems: The pressure is due to both evolution of a permanent gas and increasing vapour pressure with increasing temperature.

Vapour pressure systems are tempered in that a properly designed pressure relief system can remove latent heat at a sufficient rate to hold the temperature approximately constant at constant pressure (see Figure 3.3). (The temperature may actually rise or fall slightly at constant pressure due to changes in the liquid composition caused by the reaction and by preferential vaporisation of the more volatile components.) Because reaction rate is most strongly a function of temperature, pressure relief can control (temper) the rate of reaction for vapour pressure systems. However, care should be taken that the rate will indeed be held constant at constant temperature. For some reactions, pH dependency or autocatalysis can cause the rate to increase at constant temperature. It is also worth noting that, in some cases, tempered systems can become untempered if all the solvent boils off during the course of the runaway.

Gassy systems are untempered in that pressure relief will not control the temperature or the reaction rate. Hybrid systems can be either tempered or untempered depending on the relative rates of vapour and gas production at the chosen pressure. Lowering the pressure during relief normally increases the likelihood of tempering because the vapour pressure becomes a higher proportion of the total pressure. However, in some cases, this can also increase the likelihood that all of a solvent would be vaporised, either by the reaction itself or by external fire, before the reaction reaches completion. Hybrid systems can be treated as gassy systems if the vapour pressure is low (less than about 10% of the total pressure).

A taxonomy of the types of system for relief sizing purposes is given in Figure 4.1.

Figure 4.1 TAXONOMY OF SYSTEM TYPES FOR RELIEF SIZING



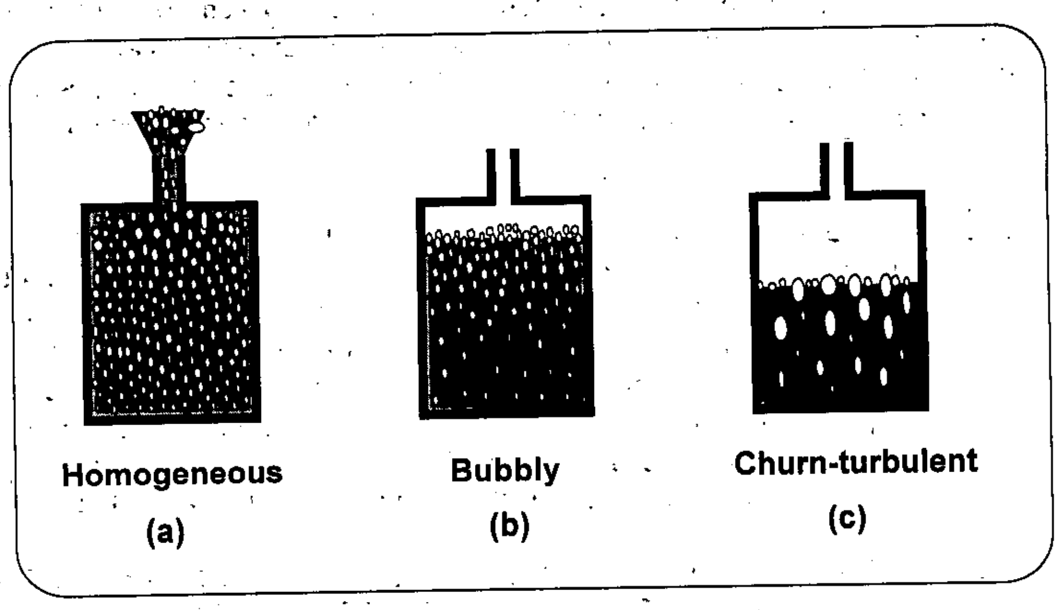
4.2.2 Determination of system type for relief sizing

The determination of the system type should be done experimentally. The experimental method will depend on the type of calorimetric equipment used. Some information is given in Annex 2.

4.3 VESSEL FLOW REGIME CLASSIFICATION

Runaway chemical reactions usually vent a two-phase mixture of liquid plus gas or vapour. The two-phase flow regime (see 4.3.1 and figure 4.2) within the venting vessel will influence the fraction of gas or vapour within this two-phase mixture. Sometimes, single-phase gas or vapour alone may be vented. It is important to determine whether the mixture relieves a two-phase mixture or a single-phase gas or vapour because this will significantly affect the required vent size.

Figure 4.2 VESSEL FLOW REGIMES



For tempered systems, the pressure relief system will almost always need to be bigger if two-phase flow occurs, and DIERS[1] recommended that two-phase relief should normally be assumed for vent sizing purposes using the type of hand calculation methods given in this Workbook. This is explained in 4.3.2, Subsection (1).

For untempered systems, it is generally conservative to assume initial single-phase gas relief followed by two-phase relief at the peak reaction rate. However, for the hand calculation method given in Chapter 7, it is safe to assume two-phase relief. This is also explained in 4.3.2, Subsection (1).

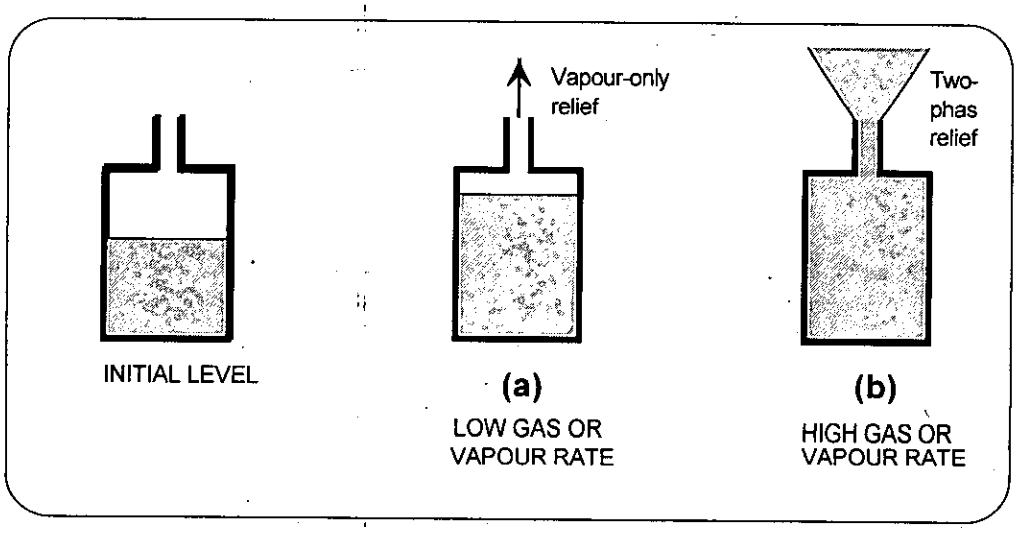
4.3.1 Level swell

Level swell is the mechanism by which runaway chemical reactions vent a two-phase mixture. When a runaway chemical reaction generates gas or vapour, bubbles are formed throughout the bulk of the liquid. Because the bubbles are buoyant, they will tend to rise through the liquid in order to disengage at the surface. However, whilst they remain in the liquid, they occupy volume and so cause the liquid level to rise or swell. If the level rises to the inlet to the pressure relief system during relief, then two-phase venting will occur.

Many reacting systems are inherently foamy, and this means that they always vent a two-phase mixture which is homogeneous, i.e. the fluid entering the vent has the same ratio of gas or vapour to liquid as the average in the vessel (see Figure 4.2(a)). Such systems would continue to vent a two-phase mixture until the vessel was empty. Very small concentrations (parts per million) of certain substances can cause inherently foamy behaviour. For this reason, (for tempered systems) an assumption of non-foamy behaviour should be regarded with care because only trace impurities (such as might occur during a runaway reaction) may cause the system to become inherently foamy. In the DIERS experimental work, using polymerisation of styrene in ethylbenzene, the polystyrene product sometimes caused the system to become inherently foamy. Adding detergent to water produced a similar effect.

Some reacting systems are not inherently foamy. In such cases, a low enough gas or vapour production rate coupled with a low enough initial fill level in the reactor will lead to single-phase, gas or vapour venting (see Figure 4.3 (a)). A higher gas/ vapour generation rate, or higher initial fill level, will cause two-phase venting (Figure 4.3 (b)) until enough liquid has been discharged that the "swelled" liquid remains in the reactor, and gas or vapour alone begins to be vented. During two-phase venting, the fluid entering the pressure relief system will contain a higher fraction of gas or vapour than for the homogeneous case produced by inherently foamy fluids.

Figure 4.3 LEVEL SWELL FOR A FLUID WHICH IS NOT INHERENTLY FOAMY (BUBBLY OR CHURN-TURBULENT FLOW)



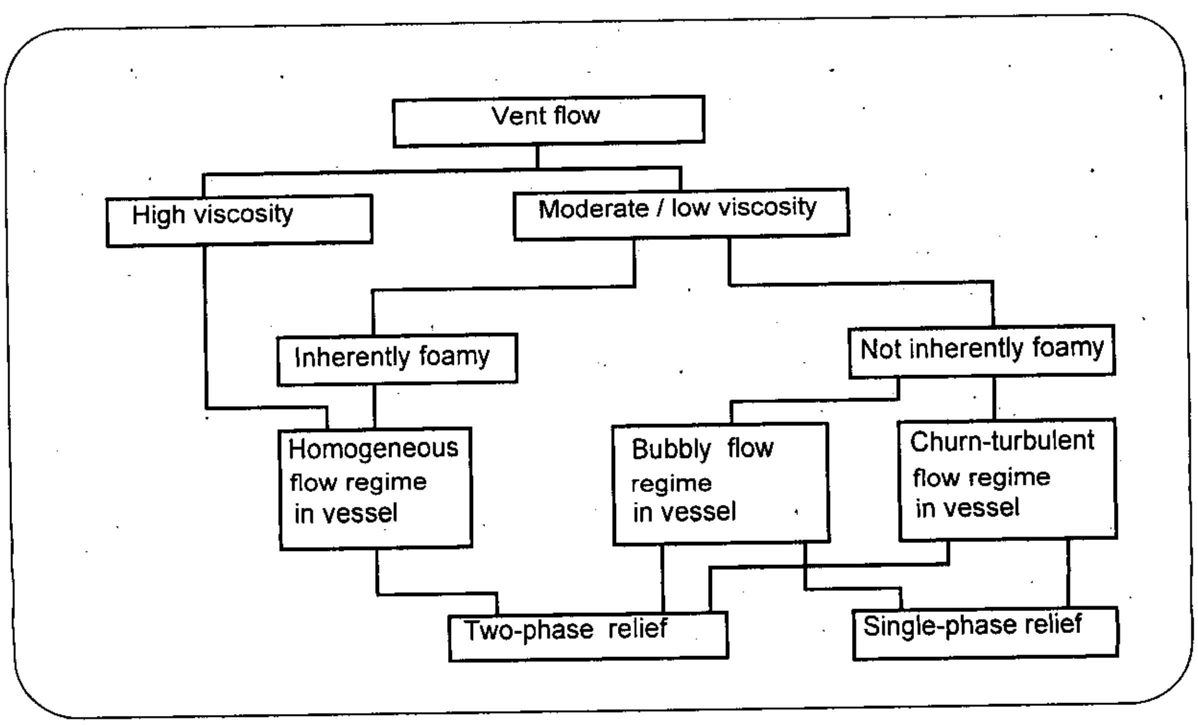
For a non-foamy system, the extent of the level swell and the fraction of gas/ vapour entering the pressure relief system, at a given gas/ vapour evolution rate, depends on the two-phase flow regime within the vessel. For non-viscous systems the two main flow regimes[1] are bubbly flow and churn-turbulent flow (see Figure 4.2 (b) and (c)). In bubbly flow, the bubbles are small and discrete and rise through the liquid relatively slowly. In churn-turbulent flow, many of the bubbles have coalesced to form larger bubbles which rise faster. For the same gas or vapour rate, the amount of level swell may be less in the churn-turbulent flow regime than in the bubbly flow regime, so that two-phase relief is more likely if the flow regime is bubbly. DIERS[1] suggest that moderately high viscosity (> 100 cP) at the flowing condition tends to result in a bubbly flow regime, whilst lower viscosity (< 100 cP) tends to result in a churn-turbulent flow regime. However, the authors are aware of exceptions to this. Two-phase flow regime transitions are notoriously difficult to predict and the best course will often be to choose the flow regime giving the worst case. This is discussed further in 4.3.2.

For high viscosity systems (greater than about 500 cP) the flow regimes are different to the above but the assumption of a homogeneous flow regime in the vessel gives good agreement with experimental results[2,3]. Pressure relief of high viscosity systems is an area of continuing research, both in the USA and Europe.

As the gas or vapour production rate increases, the flow regime may change from churn-turbulent to droplet flow, in which a fluidised bed of liquid droplets is present in the reactor (see Figure A3.1). This is of less practical interest for relief system sizing because if the gas or vapour rate is so high as to give droplet flow, the relief system size is likely to be impractically large.

A taxonomy of the different possibilities for vessel flow regimes is given in Figure 4.4.

Figure 4.4 TAXONOMY OF VESSEL FLOW REGIMES



4.3.2 Determination of vessel flow regime

The relief sizing methods described in Chapters 6, 7 and 8 make worst case assumptions about the vessel flow regime (see (1.) below) in terms of the extent to which it causes two-phase flow to enter the relief system. It is therefore not necessary to know the vessel flow regime in order to safety use these sizing methods. However, it may sometimes be desirable to determine it and calculate whether, or how much, two-phase relief would occur, because:

a) for tempered systems, if gas or vapour-only venting can be shown to occur, a smaller relief size than for two-phase relief can be obtained using the procedure in Annex 6;

b) a number of the sizing methods in Annex 4 and 5 (for tempered systems only) allow account to be taken of disengagement from two-phase relief to single-phase gas or vapour relief in order to reduce the required relief size;

c) best estimate calculations for the amount of two-phase mixture relieved are needed to reduce the size and cost of a downstream disposal system.

The worst case assumptions for relief sizing, regarding vent flow type, are described in (1.) below. If required, (2.) to (4.) describe aspects of the procedure to determine what the vessel flow regime would actually be.

(1.) <u>Worst case assumption for vent sizing</u>

For a tempered system (vapour pressure or hybrid), homogeneous two-phase venting is the worst case for vent sizing (yielding the largest required vent size). This is because, assuming the vent is at the top of the reactor, homogenous venting gives the smallest fraction of vapour entering the vent and this vapour is removing latent heat from the reacting mixture.

For an untempered system (gassy or hybrid), the worst case for vent sizing will be the flow regime which gives the slowest rate of removing liquid from the reactor, since this will cause more reactants to remain in the reactor in the later stages of the reaction when the temperature and reaction rate are at their highest. However, if the vent sizing method uses the peak gas generation rate, then it is safe to assume homogeneous two-phase venting, and this assumption is made by the relief sizing method for gassy systems given in 7.3.

(2.) <u>Deciding whether the fluid vented will be single or two-phase</u>

If required, the following method may be used to assess whether single or two-phase venting would actually be expected to occur:

(a) If the system is inherently foamy (see (3.) below), then homogeneous two-phase venting is likely to occur until the reactor is empty.

(b) If the system is not inherently foamy, then a level swell calculation (see A3.2) may be carried out to determine whether relief would be two-phase or single-phase. If this is to be done, then it will be necessary to decide whether the flow regime will be bubbly or churn-turbulent (see (4.) below). A level swell calculation may also be used to find the fill level at which initial two-phase venting would cease and single-phase venting begin. This information gives an estimate for the amount of two-phase mixture vented to the disposal system, and can also be utilised by some pressure relief system sizing methods (see Chapters 6-8 and Annex 5) to yield a smaller required vent size.

(3.) <u>Deciding whether the fluid is inherently foamy</u>

Inherent foaminess can be caused by trace quantities of certain materials, so tests should normally be done on the mixture undergoing runaway reaction. Level swell does not scale up directly, so that any small-scale blowdown test must seek to reproduce the same superficial velocity (volumetric flow divided by vessel cross-sectional area) as on the full-scale. This will be much higher than the superficial velocity otherwise produced by the runaway reaction at test-scale. Techniques for carrying out small-scale tests are discussed in Annex 2.

It may occasionally be possible to deduce from normal operation that the fluid is not inherently foamy, for example if the normal process boils the mixture (when cooling by reflux condenser) and a stable foam is not produced. However, if runaway might cause surface-active agents to be produced, then there is no substitute for testing under runaway conditions.

(4.) <u>Deciding the vessel flow regime</u>

Predicting the vessel flow regime for a two-phase mixture is difficult to do reliably (even for cases without a chemical reaction which changes the physical properties of the mixture). Thus, for relief system sizing, it is often advisable to make the worst case assumption (see (1.) above).

Further information on level swell calculations and the determination of vessel flow regimes is given in Annex 3.

4.4 VISCOSITY CLASSIFICATION

Some runaway reactions, which generate, for example, polymers or solid slurries, may produce a very high viscosity mixture in the reactor. Most of the vent sizing methods in this Workbook are limited to systems in which the flow is turbulent in the vessel and pressure relief system. If the viscosity is high, then flow may not be turbulent and it is therefore important to distinguish such systems. How high the viscosity needs to be to cause laminar, rather than turbulent flow, depends on the diameter of the pressure relief system, with laminar flow more likely in smaller diameters. See Figure 4.5.

A viscosity less than about 100 cP is unlikely to give rise to laminar flow in any practical size of relief system. The transition from turbulent to laminar flow is approximately given by[4]:

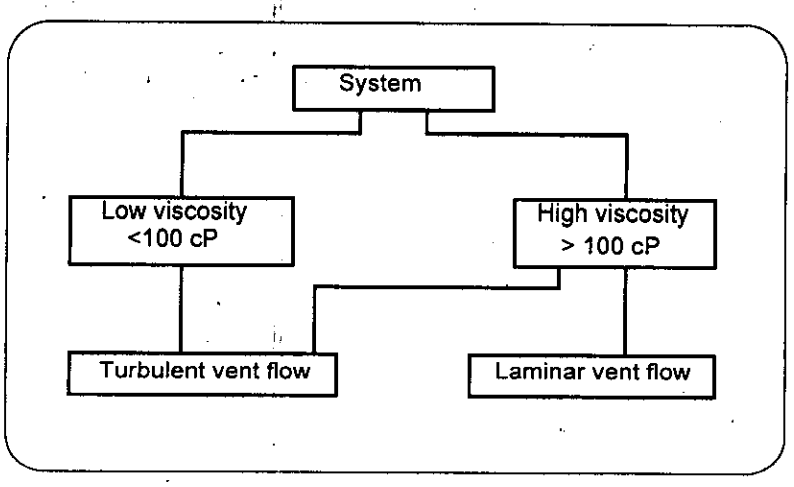
$$Re < 2000 \qquad (4.1)$$

where

$$Re = \frac{\rho u D}{\mu} \qquad (4.2)$$

However, the viscosity at which this transition takes place cannot easily be calculated because many high viscosity fluids are non-Newtonian. This means that the viscosity varies according to the rate at which the fluid is flowing. It is therefore best to carry out a small-scale test in order to determine whether or not flow will be laminar. A possible test method is given in A2.3.3. Chapter 10 gives more information on high viscosity fluids.

Figure 4.5 TAXONOMY OF VISCOSITY TYPES



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1. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter 1, AIChE/DIERS, 1992, ISBN 0-8169-0568-1

2. K Bell, S D Morris & R Oster, "Vent Line Void Fractions And Mass Flow Rates During Top Venting Of High Viscosity Fluids", J Loss Prev Process Ind, Vol 6, No 1, 31-35, 1993

3. S D Morris, K Bell & R Oster, "Top-Venting Of Flashing High-Viscosity Fluids", Chemical Engineering & Processing, 31, 297-305, 1992

4. R H Perry & D W Green (ed.), " Perry's Chemical Engineers Handbook", 7th Edition, McGraw Hill, 1997, ISBN 0-07-049841-5

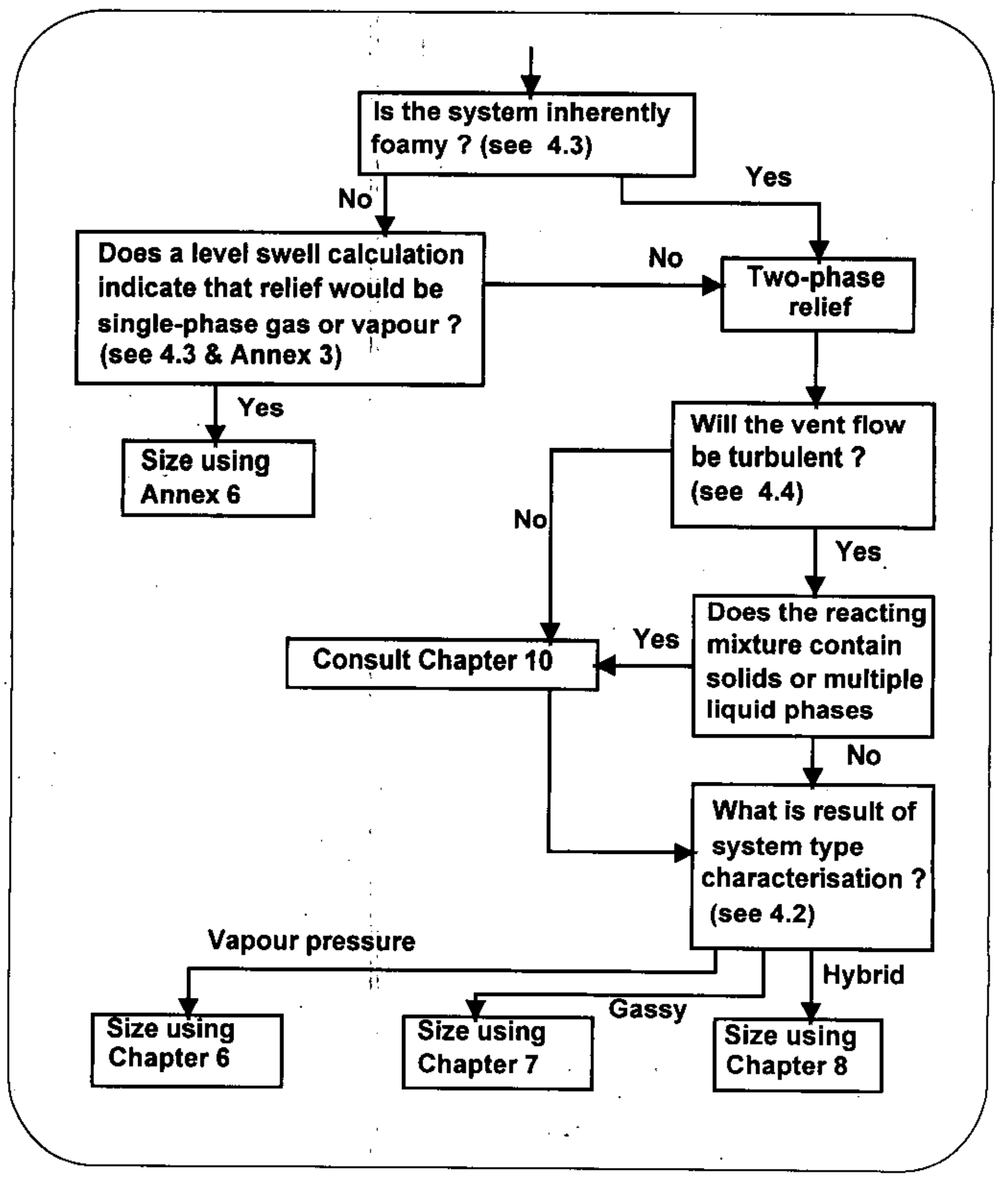
CHAPTER 5

RELIEF SYSTEM SIZING

5.1 INTRODUCTION

This chapter gives background information for the sizing of pressure relief systems for runaway chemical reactions. Detailed sizing methods are given in later Chapters and Annexes. Before using the sizing methods, it is necessary to determine the worst case design scenario (see Chapter 3) and the characteristics of the reacting system (see Chapter 4). Figure 5.1 is a decision tree which can be used to decide

Figure 5.1 DECISION TREE TO SELECT SIZING METHOD



the Chapter or Annex required for sizing, based on the system characterisation described in Chapter 4.

The Chapters indicated by Figure 5.1 give methods for calculating an average two-phase required relief rate, W (expressed as kg/s). The required relief system area, A, is calculated from:

$$A = \frac{W}{G} \qquad (5.1)$$

G, (expressed as kg/m^2s), is the average two-phase flow capacity per unit cross-sectional area of the vent-line. Methods for calculating G are given in Chapter 9. If the reacting mixture is highly viscous, contains solids or contains two separate liquid phases, additional information is given in Chapter 10.

5.2 OBJECTIVES OF PRESSURE RELIEF SYSTEM SIZING

5.2.1 Equipment requirements

The main objective of a pressure relief system is to prevent overpressurisation of the reactor and associated equipment, which includes any piping, condensers, feed vessels, sampling systems etc. which could be open to the reactor during the runaway. Currently, all such equipment which contains relevant fluids (including gases) above 0.5 barg should meet the requirements of the Pressure Systems and Transportable Gas Containers Regulations 1989[1] (PSTGC Regulations). These Regulations require the pressure system to be provided with protective devices so as to prevent danger. However, the UK Regulations are being reviewed to take account of new Regulations being drafted to enact the European Pressure Equipment Directive[2] which will enter into force in November 1999, but will be optional until May 2002. The Pressure Equipment Directive allows momentary pressure surges (such as during relief of an exothermic runaway) up to 10% above "the maximum allowable pressure" (this is the same as the design pressure). Alternatively, it requires appropriate measures to be taken to achieve an equivalent level of safety. The Directive only concerns the initial supply of equipment whereas the UK PSTGC Regulations also cover requirements for in-service examination, operation and maintenance. Consequently, the UK PSTGC Regulations will not apply to initial supply of equipment which is covered by the Pressure Equipment Directive (but the in-service requirements will still apply).

Normally such vessels will be constructed to a pressure vessel code, such as BS 5500[3] or ASME VIII[4]. Under the relevant code, the equipment will have been assigned a design pressure and many pressure vessel codes allow a temporary increase (accumulation) above this design pressure during relief, typically of 10% of the (gauge) design pressure.

Thus, in order to adequately protect the equipment, the pressure relief system should limit the pressure in the reactor (or an associated item of equipment if it has a lower design pressure) to its maximum accumulated pressure.

For some other types of emergency relief, such as dust explosion relief of relatively weak vessels, it is common practice to size the relief system to limit the pressure to that which will cause deformation but not failure of the vessel. If an explosion occurs, the deformed vessel can be replaced. Great care should be taken before applying such principles to pressure vessels for the following reasons:

a) Although a pressure vessel will usually fail at a pressure above its design pressure by virtue of factors introduced into design calculations, a number of detrimental and unquantified factors may also be present such as cracks and other defects (introduced during welding but not found during subsequent inspections), residual stresses, fatigue, creep and limitations of seals. It is difficult to take account of these factors when deciding the maximum pressure a vessel could safely withstand.

b) A pressure vessel will have been hydrostatically tested at some pressure higher than its design pressure plus permitted accumulation. However, this test is done cold (at ambient temperature) not at the elevated temperatures which could occur during a runaway. The hydrostatic test is also likely to have taken place when the vessel was new with its corrosion allowance in place.

c) The rate of pressure rise during a runaway reaction is faster than in a hydrostatic test.

d) The stored energy in a pressure vessel, should it fail, is likely to be higher and do more damage than that in a relatively weak dust handling vessel..

e) A pressure vessel is already designed to be an efficient shape for withstanding pressure. By contrast, dust handling equipment (for example) is often of such a shape (e.g. rectangular section) that deformation will increase its strength. This means that one can design dust handling equipment for an over-pressure that will cause a large deformation but not failure.

5.2.2 Pressure relief device characteristics

Pressure relief of a runaway reaction is likely to be via a bursting disc or a safety valve, or a combination of both these items. Further information about these is given in Chapter 9. For relief system sizing, it is important to know the pressure at which a relief device will open.

Bursting discs burst when the differential pressure across them exceeds a certain value, the specified bursting pressure. There is a performance tolerance on this bursting pressure, which may typically be +/- 5% or +/- 10% of the (gauge) specified bursting pressure, depending on the type of disc. The maximum pressure at which a disc may burst is therefore the specified bursting pressure plus the performance tolerance, also known as the specified maximum bursting pressure[5,6]. (A disc also has a specified minimum bursting pressure which is the specified bursting pressure minus the performance tolerance.) The expected temperature of the disc when it is at its specified bursting pressure should always be stated because the bursting pressure is temperature dependant (lower bursting pressure at higher temperatures).

Spring-loaded safety valves (relief valves) are designed to open at a set pressure. However, at the set pressure, the valve disc just begins to move off the seat. An overpressure (of usually 10%) above the (gauge) set pressure is required to give the full discharge flow. The valve manufacturer will calculate a discharge capacity for a valve under conditions specified by the user. However, many manufacturers may have difficulty doing so if the specified conditions involve two-phase flow. The valve capacity is always quoted at a particular overpressure[6,7], usually 10%.

Within this Workbook, the maximum pressure required to fully open the pressure relief device will be referred to as the "relief pressure". (Caution: some papers on relief sizing refer to "set pressure" but mean "relief pressure"). For a bursting disc, the relief pressure will be the maximum specified bursting pressure and for a safety valve, it will be the set pressure plus 10% overpressure (or whatever percentage overpressure the valve has been certified at).

It should be remembered that, for safety valve systems, a vacuum can occur in the reactor when it cools down after a runaway. It is important to take account of this in the reactor design.

5.2.3 Dynamic calculations for relief system sizing

The requirements for relief system sizing are:

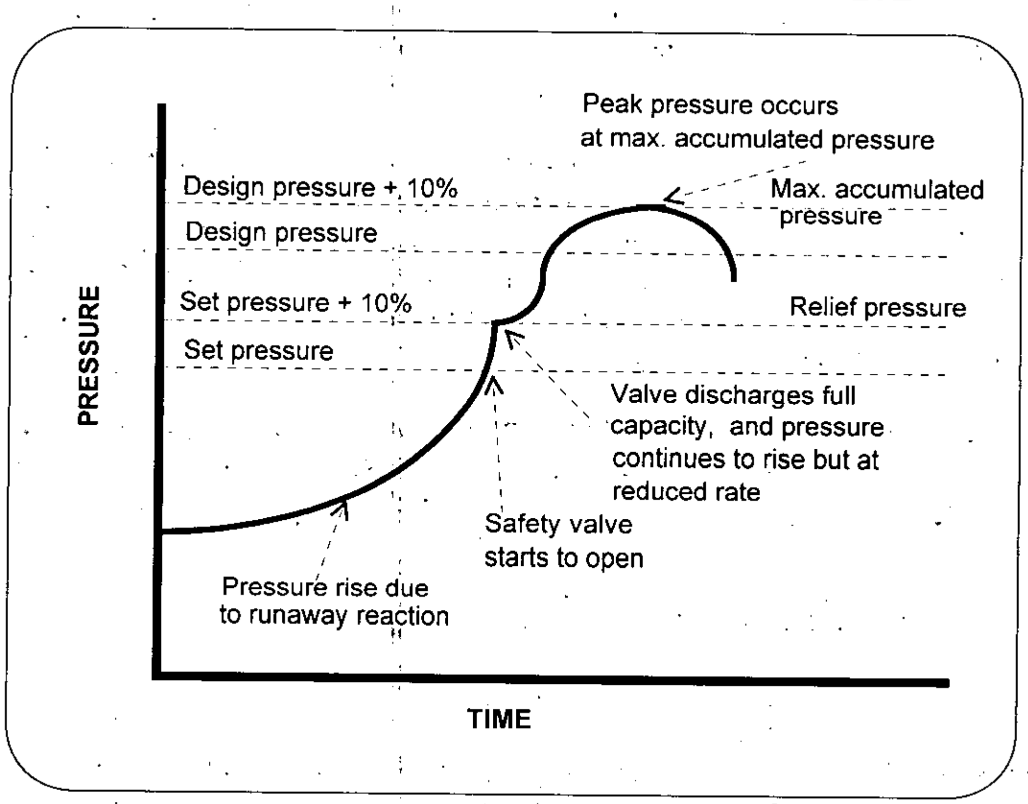
(a) that the equipment design pressure plus permitted accumulation ("maximum accumulated pressure") is not exceeded (see 5.2.1); and

(b) that the pressure relief system is as small as possible, whilst still achieving (a) above. A small relief system minimises cost, disposal requirements and the potential rate at which material could be discharged to the environment.

To achieve (b), it is necessary to use relief sizing methods that take account of the dynamics of the pressure relief event. Pressure relief systems for runaway chemical reactions usually discharge a two-phase mixture (see 4.3). If a steady-state calculation were used to size the relief system, then it would be necessary to size it for the volumetric rate of two-phase mixture equal to the volumetric rate of gas/ vapour generation at a particular point (e.g. at the relief pressure for vapour systems). This leads to very large calculated relief system sizes.

However, because the relief system is discharging a two-phase mixture, it is acting to empty the reactor. Account can be taken of this by performing a dynamic (non-steady-state) calculation, and many of the methods described later in this Workbook do this. By taking advantage of emptying, a smaller relief system size can be used. The relief pressure for this system should normally be below the design pressure plus permitted accumulation of the equipment, in order to allow time for some emptying to occur whilst the system pressure continues to rise. The minimum size of pressure relief system would be that for which the pressure peaks at the maximum accumulated pressure (see Figure 5.2).

Figure 5.2 **PRESSURE VERSUS TIME FOR A RUNAWAY REACTION WITH AN OPTIMUM SIZE OF SAFETY VALVE**



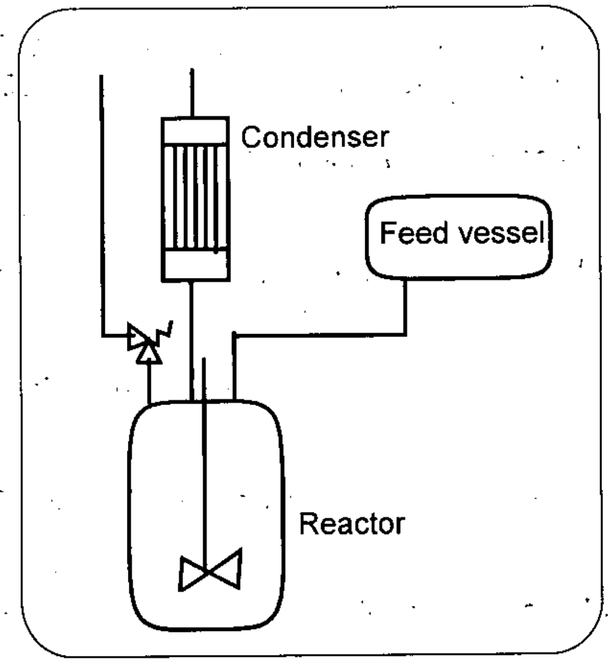
The sizing methods given in this Workbook (e.g. in Chapters 6-8) generally provide an estimate for the average two-phase required relief rate, W, during this dynamic process between the relief pressure and the maximum accumulated pressure. The relief flow area can then be obtained, using equation (5.1), given the average two-phase relief capacity per unit area, G. Chapter 9 gives calculation methods for G. An estimate of the average value of G can be provided by taking the mean of values calculated at the relief pressure and at the maximum accumulated pressure.

5.2.4 Worked example

A reaction vessel and associated equipment are as shown in Figure 5.3. The equipment design pressures (designs are to BS5500) are as follows:

Reactor	6.9 barg
Condenser	6.9 barg
Feed vessel	5.5 barg

Figure 5.3 REACTOR SYSTEM FOR WORKED EXAMPLE



The maximum operating pressure during the batch cycle is 3.2 barg and the set pressure of the safety valve is to be 4.0 barg to provide a margin in which a high pressure trip can operate and to ensure that the operating pressure is below the reseat pressure of the valve.

What are the relief pressure and maximum accumulated equipment pressure for pressure relief purposes ?

The relief pressure is that at which the pressure relief device is fully open. Safety valves typically require 10% overpressure to achieve this (N.B. this should be checked for each specific application). Thus:

Relief pressure = 1.1 x 4.0 = 4.4 barg = 5.4 bara

(Pressures are converted to bara in this example because absolute pressure is required for relief sizing calculations.)

The system design pressure is that of the weakest item of equipment which could be connected to the reactor during runaway. In this case it is the feed vessel with a design pressure of 5.5 barg. 10% accumulation is allowed during pressure relief for BS 5500. Thus,

Maximum accumulated equipment pressure = 1.1 x 5.5 = 6.05 barg = 7.05 bara

REFERENCES FOR CHAPTER 5

1. S.I. 1989 No. 2169, "The Pressure Systems and Transportable Gas Containers Regulations", HMSO, 1989, ISBN 0 11 098169 3

2. Directive 97/23/EC of The European Parliament and of The Council of 29 May 1997

3. BS 5500, "Specification for Unfired Fusion Welded Pressure Vessels", BSI, 1997

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7. BS 6759, "Safety Valves, Part 3, Specification for Safety Valves for Process Fluids", BSI, 1984

CHAPTER 6

VAPOUR PRESSURE SYSTEMS

6.1 STRATEGY FOR RELIEF SYSTEM SIZING

The logic given in Figure 5.1 can be used to check that this section is the correct one for relief system sizing for any particular case. As explained in Chapter 5, the required relief rate, W, should first be calculated using the methods described in this Chapter. A two-phase mass flow capacity per unit area, G, should then be calculated using the methods described in Chapter 9 (or Chapter 10 in special cases). The required relief flow area can then be calculated using equation (5.1).

A number of different sizing methods have been proposed for vapour pressure systems. These range from a nomograph to rigorous dynamic simulation codes[1]. In this Chapter, a sizing method by Leung[2,3] is presented, together with its conditions of applicability. Figure 6.1 illustrates a possible approach to relief system sizing, in which Leung's method is used as first choice but alternative methods are suggested if Leung's method is inapplicable or likely to oversize. This approach reflects the emphasis of this Workbook on the use of methods which can be evaluated without computer software where possible. However, the immediate use of a dynamic computer code for relief sizing (see Annex 4) may be used as an alternative to the approach shown in Figure 6.1.

The relief size obtained can be reduced by optimising the design parameters, such as relief pressure (see 6.2 below), vessel design pressure, or even changing the worst case relief scenario by designing out certain possibilities (see Chapter 3 and Annex 1).

Other relief sizing methods are available if:

a) Leung's method is inapplicable; or

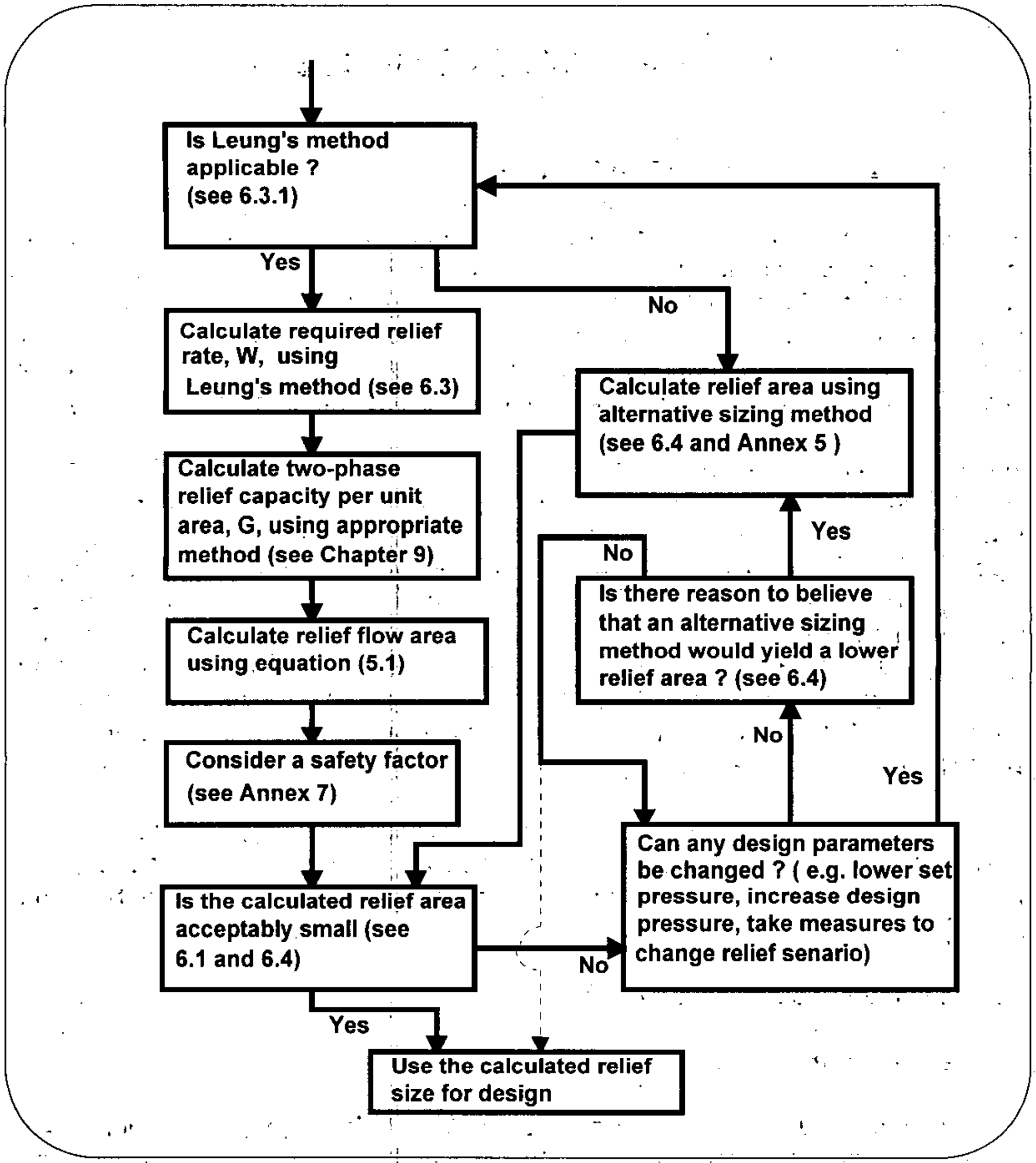
b) the calculated relief system size is unacceptably large (e.g., if it is only a little larger than an existing relief system), and there is reason to believe that another applicable method would yield a smaller size. This is amplified in 6.4 below.

6.2 CHOICE OF DESIGN PARAMETERS

6.2.1 The importance of using a low relief pressure

The relief pressure is defined in this Workbook as that at which the relief device is certain to be fully open (see 5.2.2).

Figure 6.1 STRATEGY FOR RELIEF SYSTEM SIZING FOR VAPOUR PRESSURE SYSTEMS



For a vapour pressure system (and any other tempered system) which is to relieve a two-phase mixture, there are two reasons why a low relief pressure is beneficial:

a) For most exothermic runaway reactions, the reaction rate (and heat release rate) increases exponentially with temperature. For a vapour pressure system, a low relief pressure means a low relief temperature and hence a relatively low rate of heat release. The relief area required is directly proportional to the rate of heat production by the reaction.

b) For a relief system venting a two-phase mixture, pressure relief acts to remove reactants from the reactor. A low relief pressure allows a greater margin between the relief pressure and maximum accumulated pressure, and advantage is taken of this by the sizing methods to yield a smaller relief area (see 5.2.3).

Consequently, it is normally recommended that the relief pressure be chosen as low as possible. This needs to be balanced with the need to provide a suitable margin between the set pressure or minimum specified bursting pressure and the highest normal operating pressure so that spurious operation of the relief device is avoided. (Manufacturers of relief devices can advise on this.) Also, in some cases, it may be beneficial to set a high relief pressure where a first runaway reaction can be contained, but a subsequent slow decomposition reaction (at higher temperature) must be vented.

6.2.2 Choice of relief device

The choice between using a safety valve or bursting disc for tempered systems does not affect the relief device size. However, it may have an effect on the size of disposal system required. A safety valve will minimise two-phase relief by not allowing depressurisation, whereas a bursting disc almost guarantees two-phase relief due to depressurisation. Other factors influencing the choice between bursting discs and safety valves are given in references 5 and 6.

6.3 LEUNG'S METHOD FOR RELIEF SYSTEM SIZING FOR VAPOUR PRESSURE SYSTEMS

Leung's method is given in 6.3.2 below. The method is an approximate solution to the differential mass and energy balances for the reactor during relief and takes account of both emptying via the relief system and the tempering effect of vapour production due to relief. The method makes use of adiabatic experimental data for the rate of heat release from the runaway reaction (see Annex 2). Nomenclature is given in Annex 10.

6.3.1 Conditions of applicability of Leung's method

This particular Leung method[2,3,6] (Leung has produced several different relief sizing methods for different cases) is a solution to the material and energy balances for a tempered relieving runaway reaction under homogeneous venting conditions. The method makes the following assumptions:

a) The mass of the vapour phase in the reactor is negligible in comparison with the mass of the liquid phase.

b) It is reasonable to represent all physical properties by average values, between the relief pressure and the maximum pressure.

c) The pressure will be controlled if the temperature is controlled, i.e. the system is tempered and does not become significantly less volatile as relief proceeds; also the reaction rate is controlled by temperature rather than other factors such as pH. Moderate deviation from this assumption can be accommodated (see later in this section).

d) It is reasonable to represent the heat generation rate per unit mass of reactants, q, by an average value between the relief pressure and the maximum pressure (see later in this section).

e) It is reasonable to represent the mass vent capacity per unit area (for two-phase venting), G, by an average value between the relief pressure and the maximum pressure. G is taken as being constant over the pressure range between the relief pressure and the maximum permitted pressure. This may not be valid at high overpressures (see later in this section).

f) The material vented from the reactor is a homogeneous two-phase mixture, i.e. it contains the same vapour/ liquid ratio as the average for the reactor, at any given time. (For a tempered system, this is a safe assumption for relief sizing for relief from the top of the reactor).

g) There is no heat gain or heat loss from the reactor contents. (It is safe to use the method if the contents of the real reactor are subject to heat loss. In the case of heat gain, from process heating or external fire, the method is a good approximation if the total rate of heating is primarily from the exothermic reaction at the relief pressure, and if the calorimetric results include heating of the sample to simulate the external heating throughout the course of the runaway. Otherwise, see 6.4 below.)

h) Apart from the relief stream, the reactor is a closed vessel. Thus, the rate of any continuing feed stream is assumed to be negligible.

i) Vapour/ liquid equilibrium is maintained in the reactor during the relief process. (Although it is recognised that this is unlikely to be true in practice, it is believed safe to assume this for relief sizing[7].)

j) The liquid phase is incompressible. (This is a safe assumption for relief sizing.)

Leung's method (as given in equation (6.5) below) is applicable if all the above assumptions are true. Assumption (d) above, regarding the use of an average rate of heat release, tends to be the most limiting in terms of the maximum difference that can be allowed between the relief pressure and the maximum pressure. The absolute overpressure (often referred to simply as the "overpressure") has been sometimes used to characterise this. This is given by:

Absolute overpressure = $\frac{(P_m - P_R)}{P_R}$ x 100% (6.1)

The absolute overpressure is different from the overpressure of a safety valve which is expressed in terms of gauge pressures. It was originally recommended by Leung[3] that the arithmetic mean be used for the heat release rate per unit mass:

$$\bar{q} = 0.5 C_f \left[\left(\frac{dT}{dt}\right)_R + \left(\frac{dT}{dt}\right)_m \right] \qquad (6.2)$$

If equation (6.2) is used, then comparison with dynamic simulation[3] suggested that Leung's method would increasingly oversize at absolute overpressures above 50%. Provided the rate of temperature rise due to the runaway continues to increase at high overpressures, the arithmetic mean (equation 6.2) overestimates the true average q.

Leung[2] has more recently suggested an alternative average for q to help overcome this problem at high absolute overpressures:

$$\bar{q} = C_f \frac{\Delta T}{\Delta t_B} \qquad (6.3)$$

where Δt_B, the Boyle time, is the time taken in an adiabatic closed vessel for the pressure to rise from the relief pressure to the maximum accumulated pressure, and can be measured in a closed vessel experiment. The use of equation (6.3) makes Leung's method approach the results of the modified Boyle method (see A5.13) at high overpressures.

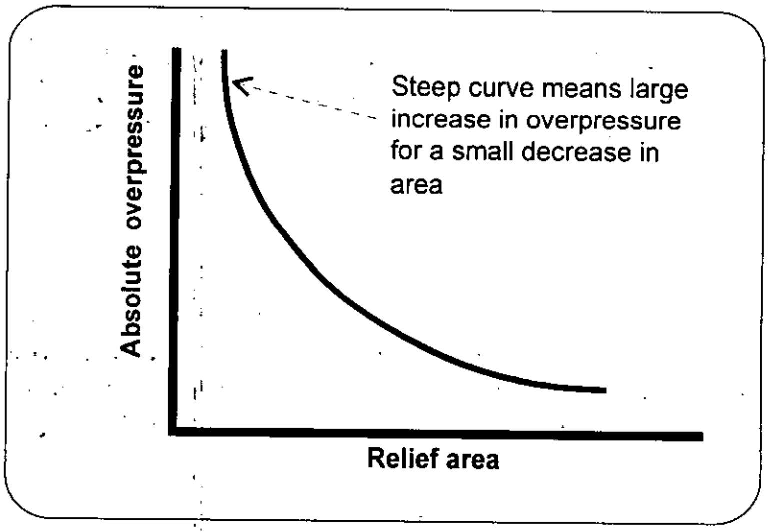
An alternative criterion to equation (6.1) for the applicability of Leung's method at high overpressures is given by CCPS[4]:

$$\frac{(dT/dt)_m}{(dT/dt)_R} \leq 2 \qquad (6.4)$$

At high absolute overpressure (> 50%), or when criterion (6.4) is met, there is an increased likelihood that the pressure turnover (i.e. the point at which the pressure stops rising and begins to fall) occurs because the reaction has reached completion, rather than due to a combination of emptying and tempering as is assumed by Leung's method. In such cases, Leung's method will tend to increasingly oversize. This is because the reaction will reach completion at a lower temperature/ pressure in a real reactor which experiences some heat losses, than is given by adiabatic calorimetric data suitably corrected for thermal inertia (see A2.7.2).

Care should be taken if high absolute overpressures are used, because the maximum pressure becomes increasingly sensitive to the installed relief area[6] (see Figure 6.2), such that a slight undersizing of the relief system causes a maximum pressure much higher than that designed for. Thus, there is more need for a safety factor (see Annex 7) or the use of more accurate sizing methods (see 6.4) at high overpressures.

Figure 6.2 RELATIONSHIP BETWEEN ABSOLUTE OVERPRESSURE AND RELIEF AREA



Assumptions (b) to (d) above will render Leung's method inapplicable if some step-change in behaviour occurs within the pressure range from the relief pressure to the maximum pressure. This could be due, for example, to a different reaction occurring. Assumptions (b) and (c) may not be valid if there are large changes in the physical properties of a wide boiling mixture as the more volatile components are preferentially boiled off. If the mixture exhibits a boiling range then q should be evaluated using the maximum temperatures in the ranges corresponding to the relief pressure and the maximum accumulated pressure.

6.3.2 Leung's method

Once it has been checked that the method is applicable (see above), it can be used for relief system sizing. Leung's method is[2,3,6]:

$$W = \frac{m_R \bar{q}}{\left[\left(\frac{V}{m_R}\frac{h_{fg}}{v_{fg}}\right)^{0.5} + \left(C_f \Delta T\right)^{0.5}\right]^2} \qquad (6.5)$$

The average value of q can be calculated using equations (6.2) or (6.3) above and adiabatic experimental data which should be corrected to a thermal inertia of 1 (see Annex 2). The temperatures corresponding to the relief pressure and maximum accumulated pressure are obtained from vapour pressure data. The temperature difference between the relief pressure and the maximum pressure, ΔT, can also be obtained from experimental data, as described in A2.4.

The physical properties, latent heat (h_{fg}), specific volume change (v_{fg}), and liquid specific heat capacity (C_f), are all required to evaluate the method. Liquid specific heat capacity can usually be measured quite easily. Data are required from the literature or a physical properties database for the latent heat and latent specific volume change, which is given by:

$$v_{fg} = \frac{1}{\rho_g} - \frac{1}{\rho_f} \tag{6.6}$$

h_{fg} and ρ_g should be evaluated using the vapour composition (which will be rich in the more volatile components), and averaged between the relief pressure and maximum pressure[7].

The required relief flow area can be evaluated using equation (5.1) knowing the two-phase mass flow rate per unit cross-sectional area of the relief system, G:

$$A = \frac{W}{G} \tag{5.1}$$

G can be evaluated using any applicable method and guidance is given in Chapter 9. The original version of Leung's method[3] recommended that G be calculated at the relief pressure in order to be conservative. However, later versions allow an average value of G, between the relief pressure and the maximum accumulated pressure to be used. For example, DIERS[6] gives the following equation to obtain an average value of G from that at the relief pressure:

$$G = G_R\left(1 + 0.5\left(\frac{P_m - P_R}{P_R}\right)\right) \tag{6.7}$$

Alternatively, the mean of G (calculated at the relief pressure) and G (calculated at the maximum accumulated pressure) can be used. Since Leung's method assumes that the reactor contents are homogeneous during relief, the consistent assumption for the vapour fraction at inlet to the relief system (needed to calculate G) is that it is the same as the average for the reactor, i.e. at the inlet to the relief system the void fraction is given by:

$$\alpha = \frac{V - \frac{m_R}{\rho_f}}{V} \tag{6.8}$$

A worked example of the use of Leung's method is given in 6.5 below.

6.3.3 Alternative version of Leung's method (and associated applicability)

For some reacting mixtures, it is difficult to find physical property data. An alternative version of Leung's method[3] makes use of the Clausius-Clapeyron thermodynamic relationship to give a formula in which all the data required can be measured experimentally. The Clausius-Clapeyron relationship ($T(dP_v/dT) = h_{fg}/v_{fg}$) only holds for ideal single-component systems, and so its use introduces the following additional conditions of applicability:

a) The vapour phase should be an ideal gas.

b) The vapour/ liquid equilibrium should be ideal.

c) The mixture should behave like a single pseudo-component (this will not be the case for mixtures with a wide boiling range).

These conditions are most likely to be met at relatively low pressure (less than, say, 5 bar). If there is any doubt over the applicability of the Clausius-Clapeyron relationship, it is suggested that a different method be used (see 6.3.2 and 6.4).

The alternative version of Leung's method is :

$$W = \frac{m_R \bar{q}}{\left[\left(\frac{VT}{m_R}\frac{dP_v}{dT}\right)^{0.5} + \left(C_f \Delta T\right)^{0.5}\right]^2} \qquad (6.9)$$

The slope of the vapour pressure versus temperature curve, dP_v/dT, can be obtained experimentally (see Annex 2). The most accurate method is to take tangents to the pressure (corrected for the presence of pad gas) versus temperature data from a closed test, or to fit the data to the following relationship[6]:

$$\ln P_v = a - \frac{b}{T} \qquad (6.10)$$

$$\frac{dP_v}{dT} = \frac{bP}{T^2} \qquad (6.11)$$

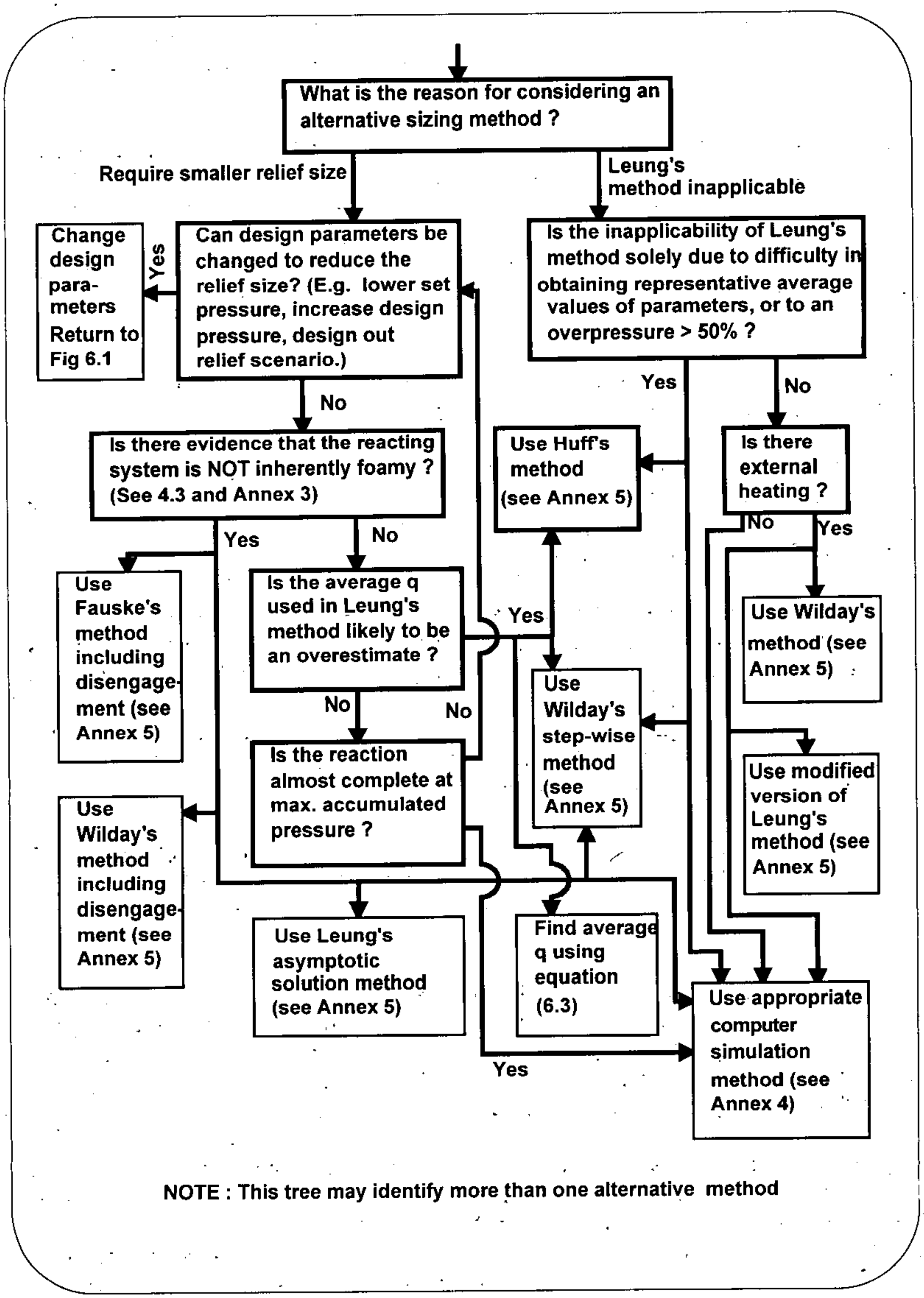
An example of the use of equation (6.11) is given in 6.5 below.

The required relief flow area can be evaluated using equation (5.1) knowing the two-phase mass flow rate per unit cross-sectional area of the relief system, G. This can be evaluated using any applicable method and guidance is given in Chapter 9.

6.4 ALTERNATIVE RELIEF SYSTEM SIZING METHODS FOR VAPOUR PRESSURE SYSTEMS

An alternative relief sizing method to Leung's method may be needed, either if both versions of Leung's method are inapplicable, or if they yield unacceptably large relief sizes (see below). The decision tree in Figure 6.3 can be used to select possible alternative relief sizing methods. Generally, the alternative methods, when applicable, may yield more accurate (less conservative but still safe) estimates of the required relief size, but at the cost of increased design time and, sometimes, the need for additional data. The strategy shown in Figure 6.3 reflects the emphasis in this Workbook on relief sizing methods which do not require computer software. Computer simulation may be used at an earlier point than is shown in Figure 6.3 (see 1.2 and Annex 4).

Figure 6.3 DECISION TREE FOR SELECTING ALTERNATIVE TWO-PHASE RELIEF SIZING METHODS FOR VAPOUR PRESSURE SYSTEMS



NOTE : This tree may identify more than one alternative method

6.4.1 Alternative methods to reduce the relief system size

If an expensive downstream disposal system is to be provided, it is likely to be cost effective to seek the minimum safe relief size. Also, if the relief system size on a multipurpose plant is being checked for a new duty, there will be an incentive to demonstrate, if possible, that the existing relief system is adequate.

In such cases, the greatest reduction in required relief size is likely to be achieved by applying the principles of inherent safety[8-10] to design out the possibility of runaway or, at least, the worst relief scenarios. Where this is not viable, prevention of runaway may, in some cases, be achieved by control measures of sufficient safety integrity[11,12]. Further discussion is given in Annex 1. Changing design parameters, such as by reducing the set pressure, can also lead to a smaller required relief size.

If it is still desired to reduce the calculated size of the relief system, then more accurate calculation methods may give rise to a smaller relief size.

Significant reduction in relief system size may be possible if the reacting system can be shown not to be inherently foamy (see 4.3 and Annex 2) so that account can be taken of vapour/ liquid disengagement within the reactor. There are two types of method which take advantage of this:

a) Methods which assume homogeneous two-phase flow from the reactor until the mass remaining in the reactor is low enough that vapour-only flow is predicted by the level swell methods given in Annex 3. Examples are Fauske's method taking account of disengagement, Wilday's method taking account of disengagement, and Wilday's step-wise method (if a test for disengagement is included). These are all detailed in Annex 5, together with any necessary applicability checks for the methods.

b) Methods which take account of partial disengagement during two-phase relief, so that the vapour fraction entering the relief system is greater than the average for the reactor. Examples are Leung's asymptotic solutions (see Annex 5) and computer simulations (see Annex 4).

Type (b) methods above are likely to yield smaller relief sizes than type (a). However, great care is needed when using type (b) methods to ensure that they do not undersize, e.g. through the inadvertent choice of a flow regime which does not occur in practice. Consequently, a higher safety factor might be expected for type (b) methods than type (a) methods. See Annex 7.

Leung's method is also likely to overestimate the required relief size if the average value of q has been overestimated. This may be the case if average q has been obtained as an arithmetic mean (equation (6.2)) and the overpressure is high. Leung's method will also overestimate in cases where the small-scale testing (see Annex 2) suggests that the reaction will be almost complete at the maximum pressure allowed during relief. These cases are discussed further below.

6.4.2 Alternative methods because of inapplicability of methods

If Leung's method is inapplicable due to the presence of external heating, then alternative hand calculation methods are given in Annex 5 or a computer simulation could be used (see Annex 4). In either case, the thermal data should be obtained in a small-scale test which also simulates the external heat input.

One reason for Leung's method being inapplicable is difficulty in finding representative average values of the parameters in the equation, between the relief pressure and the maximum accumulated pressure. This may be due to a high overpressure, or due to discontinuities in the behaviour, due to multiple reactions or mixtures with a wide boiling range such that the more volatile components boil off completely. Huff's method (see Annex 5) is more tolerant of high overpressures than Leung's method. Also, in such cases, Wilday's step-wise method (see Annex 5) may be useful. This method divides the total pressure range into smaller steps over which it is more reasonable to provide average values of parameters.

One example of a discontinuity is a drop in reaction rate due to depletion of reactants as the reaction nears completion. In this case, the step-wise method can still be used, but will tend to oversize. This is because heat losses in the full-scale reactor will cause the reaction to reach completion at a lower temperature/ pressure than was measured in an adiabatic small-scale test, corrected for thermal inertia (see Annex 2). It is not recommended to attempt to take account of heat losses from the full-scale reactor in sizing the relief system (e.g. by modelling them within a computer simulation). This is because a slight overestimation of the rate of heat loss could cause a large underestimation of the relief size required.

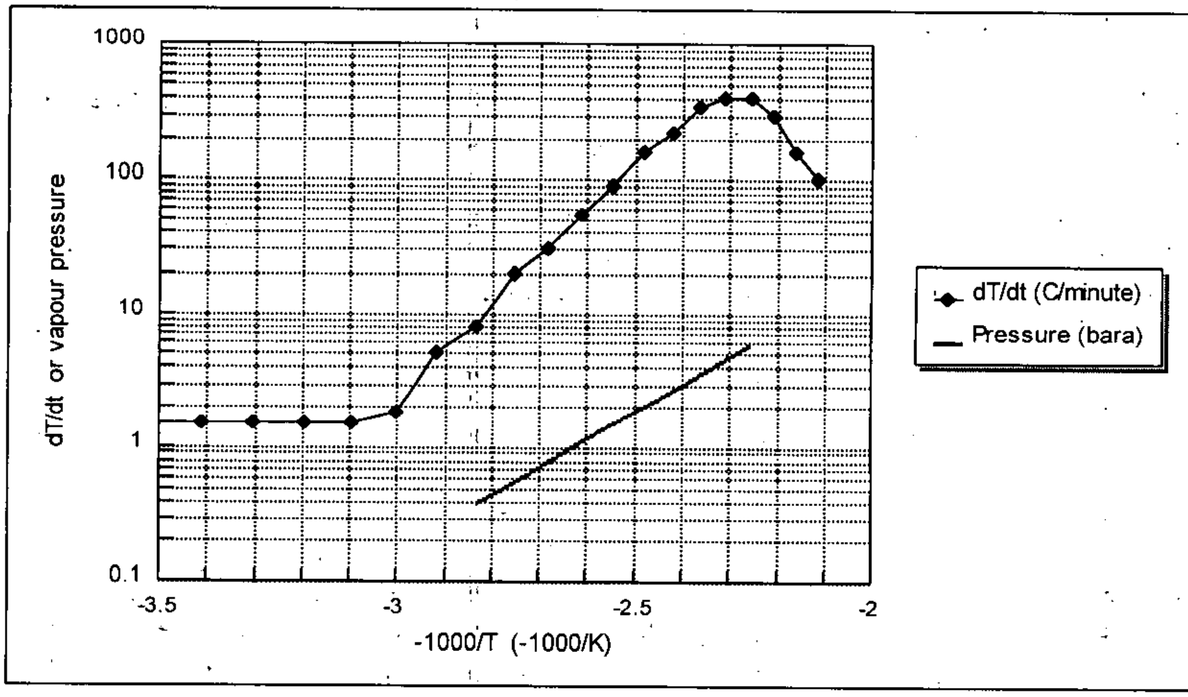
Where the Leung methods are inapplicable, a detailed computer simulation can be used to sizing the relief system (see Annex 4). In such cases, care should be taken that the computer code models all necessary features of the relieving runaway reaction. Therefore computer simulations are best carried out by competent specialists.

6.5 WORKED EXAMPLE OF RELIEF SYSTEM SIZING FOR A VAPOUR PRESSURE SYSTEM USING LEUNG'S METHOD

6.5.1 Description of example problem

A reactor has a volume of 2 m^3. The worst case runaway reaction has been identified and the data from a suitable adiabatic, low thermal inertia test, with a thermal inertia (ϕ) of 1.05, is given in Figure 6.4. Under these conditions, the reactor would contain 793 kg of reactants. The reacting system is a vapour pressure system. It is desired to relieve the runaway via a safety valve, if possible, with a set pressure of 0.91 barg (relief pressure of 1.0 barg = 2.0 bara). Evaluate the required relief size for an overpressure of 30% of the absolute relief pressure, which gives a maximum pressure of 2.6 bara = 1.6 barg.

Figure 6.4 EXPERIMENTAL DATA FOR WORKED EXAMPLE



The vapour pressure data (from a physical properties database capable of carrying out multi-component estimations) has been plotted as a straight line on Figure 6.4. This allows the temperatures at the relief pressure and maximum pressure to be read off. The rates of temperature rise at these pressures can also be read off. These values are given in Table 6.2.

Table 6.2 Temperature and dT/dt values for worked example

Pressure (bara)	2	2.6
-1000/T (-1000/K)	-2.51	-2.43
Temperature (°C)	126	138
dT/dt (°C/minute)	140	200

From a knowledge of these temperatures, together with the composition of the reacting mixture, physical property values can be obtained, e.g. from a suitable physical properties package which estimates properties for multi-component mixtures. (It may often be sufficient to estimate the properties at the initial reactant composition, or to take average values between reactant and product compositions.) Table 6.3 gives these physical property values, together with average values between the relief pressure and maximum accumulated pressure.

Table 6.3 Physical property data for worked example

Pressure (bara)	2	2.6	Average
Temperature (K)	399	411	
Liquid density (kg/m^3)	951	937	944
Liquid specific heat (kJ/kg K)	2.23	2.26	2.245
Latent heat (kJ/kg)	1,050	920	985
Vapour density (kg/m^3)	2.18	2.83	2.51

6.5.2 Relief sizing using Leung's method

The average value of q can be calculated as shown below. Because the thermal inertia of the calorimeter is low and the reaction is not nearing completion at the maximum accumulated pressure (the temperature corresponding to the maximum accumulated pressure is still on the straight-line portion of Figure 6.4), a simple correction can be made by multiplying the measured rate of temperature rise by the thermal inertia (see A2.7.2).

$$\bar{q} = 0.5C_f\left[\left(\frac{dT}{dt}\right)_R + \left(\frac{dT}{dt}\right)_m\right] \qquad (6.2)$$

$$\bar{q} = 0.5x2245\left[\left(\frac{140x1.05}{60}\right) + \left(\frac{200x1.05}{60}\right)\right] = 6679\ W/kg$$

The average value of v_{fg} can be found :

$$v_{fg} = \frac{1}{\rho_g} - \frac{1}{\rho_f} \qquad (6.6)$$

At 2.0 bara $\quad v_{fg} = \frac{1}{2.18} - \frac{1}{951} = 0.4577\ m^3/kg$

At 2.6 bara $\quad v_{fg} = \frac{1}{2.83} - \frac{1}{937} = 0.3523\ m^3/kg$

The average value of v_{fg} is 0.4050 m^3/kg

Leung's method can now be used for sizing:

$$W = \frac{m_R\,\bar{q}}{\left[\left(\frac{V}{m_R}\frac{h_{fg}}{v_{fg}}\right)^{0.5} + \left(C_f\,\Delta T\right)^{0.5}\right]^2} \qquad (6.5)$$

$$W = \frac{793 \text{ x } 6679}{\left[\left(\frac{2}{793}\frac{985000}{0.4050}\right)^{0.5} + (2245 \text{ x } (411-399))^{0.5}\right]^2} = 90.1\ kg/s$$

In order to calculate a relief flow area, the two-phase mass flow rate per unit area, G, needs to be calculated. Since relief is to be via a safety valve, friction can be neglected and the equilibrium rate model (ERM) can be used to calculate G (see 9.4.2):

$$G = \left(\frac{dP_v}{dT}\right)_0 \sqrt{\frac{T_0}{C_{f0}}} \qquad (9.3)$$

dP_v/dT can be obtained from equation (6.11):

$$\frac{dP_v}{dT} = \frac{bP}{T^2} \qquad (6.11)$$

where b is the slope of the graph of lnP vs -1/T. This can be obtained by reading two points from the vapour pressure line in Figure 6.4.

P = 3 bara at (-1000/T) = -2.4; T = 416.7 K
P=0.75 bara at (-1000/T) = -2.7; T = 370.3 K

Thus, $b = \dfrac{\ln\left(3x10^5\right) - \ln\left(0.75x10^5\right)}{-\left(\frac{-1}{416.7}\right) - -\left(\frac{1}{370.3}\right)} = 4610$

At 2.0 bara,

$$\frac{dP_v}{dT} = \frac{4610x2.0x10^5}{399^2} = 5791\ N/m^2K \qquad (6.11)$$

$$G = 5791x\sqrt{\frac{399}{2230}} = 2450\ kg/m^2s \qquad (9.3)$$

By the same method, at 2.6 bara, G = 3026 kg/m^2s
Average G = 2738 kg/m^2s

Using the alternative version of the simplified ERM :

$$G = \frac{h_{fg0}}{v_{fg0}\sqrt{C_{f0}T_0}} \qquad (9.4)$$

At 2.0 bara $\quad G = \dfrac{1050000}{0.4577\sqrt{2230x399}} = 2432\ kg/m^2s$

Using the same method, at 2.6 bara, G = 2710 kg/m^2s
Average G = 2571 kg/m^2s

The difference between the two methods may be due to deviations from the applicability of the Clausius-Clapeyron equation (for the alternative method). Therefore, G has been taken from equation (9.3) (the average value of G of 2738 kg/m^2s between the relief pressure and maximum accumulated pressure) for sizing purposes. However, this must be multiplied by the discharge coefficient of the safety valve. CCPS[4] suggest that a discharge coefficient appropriate for gas/ vapour flow through a safety valve can be used for two-phase flow provided the flow is choked (see Chapter 9). Choked flow can be expected in this case because a critical pressure ratio greater than 0.5 is usual for flashing two-phase flow (see Figure A8.2 at Omega > 1). The de-rated safety valve discharge coefficient for vapour flow is 0.87 and thus G = 0.87 x 2738 = 2382 kg/m²s.

The required relief flow area can now be calculated using equation (5.1):

$$A = \frac{W}{G} = \frac{90.1}{2382} = 0.0378 \quad m^2 \qquad (5.1)$$

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CHAPTER 7

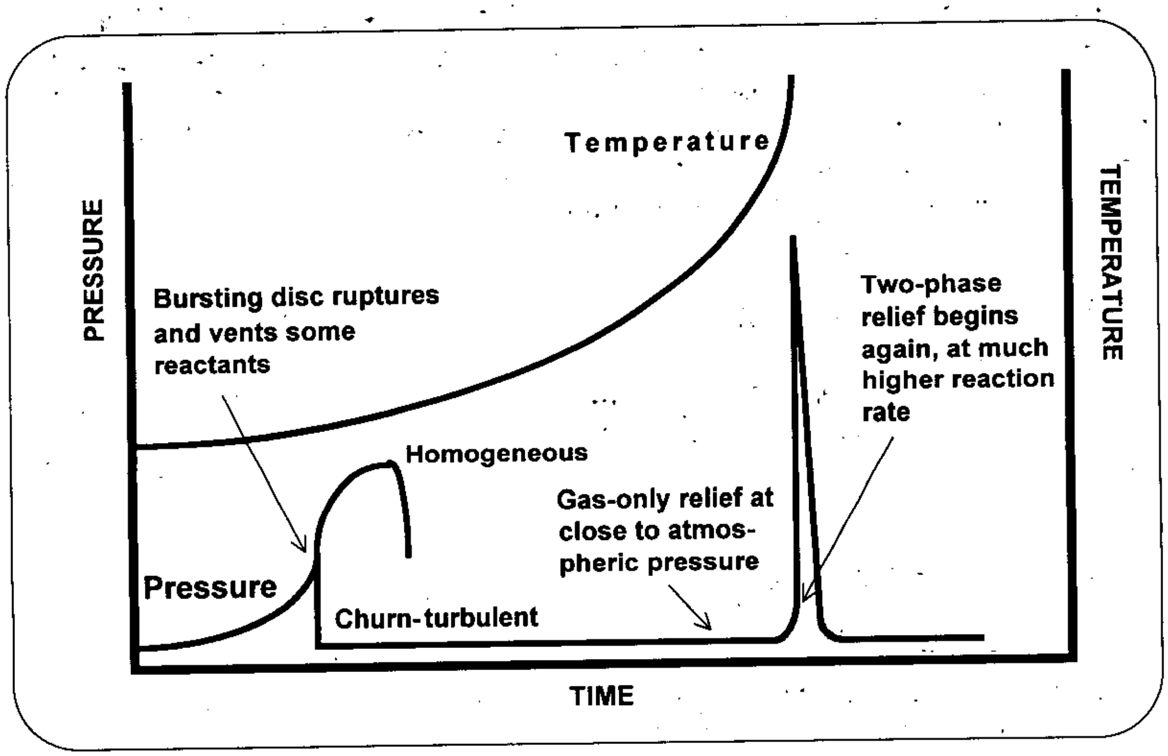
GASSY SYSTEMS

7.1 STRATEGY FOR RELIEF SYSTEM SIZING

The logic given in Figure 5.1 can be used to check that this section is the correct one for relief system sizing for any particular case.

Gassy systems are untempered. This means that the operation of the relief system cannot control the rate of the runaway reaction, but simply acts to remove material from the reactor. For untempered systems, homogeneous flow in the reactor (see 4.3) is not the worst case because it causes early emptying of the reactor, before the temperature and reaction rate get too high. The worst case is normally the vessel flow regime that results in the slowest rate of removing liquid from the reactor (i.e. the most vapour/ liquid disengagement). This is usually the churn-turbulent flow regime (see 4.3). In this case, a two-phase mixture may be relieved initially, followed by gas only relief. Material may then remain in the reactor and continue to run away, reaching a temperature approaching that at the adiabatic temperature rise for the reaction, with the corresponding very high reaction rate. As the gas evolution rate increases, this can cause two-phase relief to be re-established, and a considerable rise in the system pressure may occur (see Figure 7.1).

Figure 7.1 POSSIBLE BEHAVIOUR OF A GASSY SYSTEM DURING RELIEF



Although churn-turbulent flow in the reactor is usually a worst case (giving rise to the greatest amount of vapour/ liquid disengagement), the relief system can be sized on the basis of homogeneous or bubbly flow if they can be shown to occur. Section 4.3.2 (4.) discusses the determination of the vessel flow regime. However, the method described in 7.3 is independent of the vessel flow regime.

For an untempered system, the relief sizing method should normally use the peak reaction rate. Great care must be taken if the relief sizing method makes use of the reaction rate when the relief system first operates, as this is less than the peak rate. In such cases, there is danger that conditions later during the relief process will be worse, and require a larger relief size.

For untempered systems, it is worthwhile considering the use of bottom venting (dumping), rather than relief from the top of the reactor, since this is likely to require a smaller system. In either case, the safe disposal of the vented material should be considered (see Chapter 11). Relief from the bottom of the reactor may be a poor option if a relief system is also required at the top of the reactor for other process reasons. Operation of the relief system at the top of the vessel would reduce the pressure available to remove the contents of the reactor via the bottom relief system. This is discussed further below.

A number of sizing methods are available for gassy systems, and Figure 7.2 is a decision tree that can be used to aid selection. A single hand calculation method for top venting and a single method for bottom venting are given in this Chapter.

The sizing equation given here for top venting can sometimes give rise to conservative relief sizes because it combines a number of conservative assumptions. In some cases, this method yields relief sizes that are so large that they will not fit onto the reactor. One option for such reactions is to change the process, if possible, using inherent safety principles, to eliminate the possibility of the runaway (see Annex 1). Alternatively, some other sizing methods are available that can reduce the conservatism of the calculated relief size, at the cost of additional design and/or experimental work. These alternative methods are identified in Figure 7.2 and are given in Annexes 4 and 5.

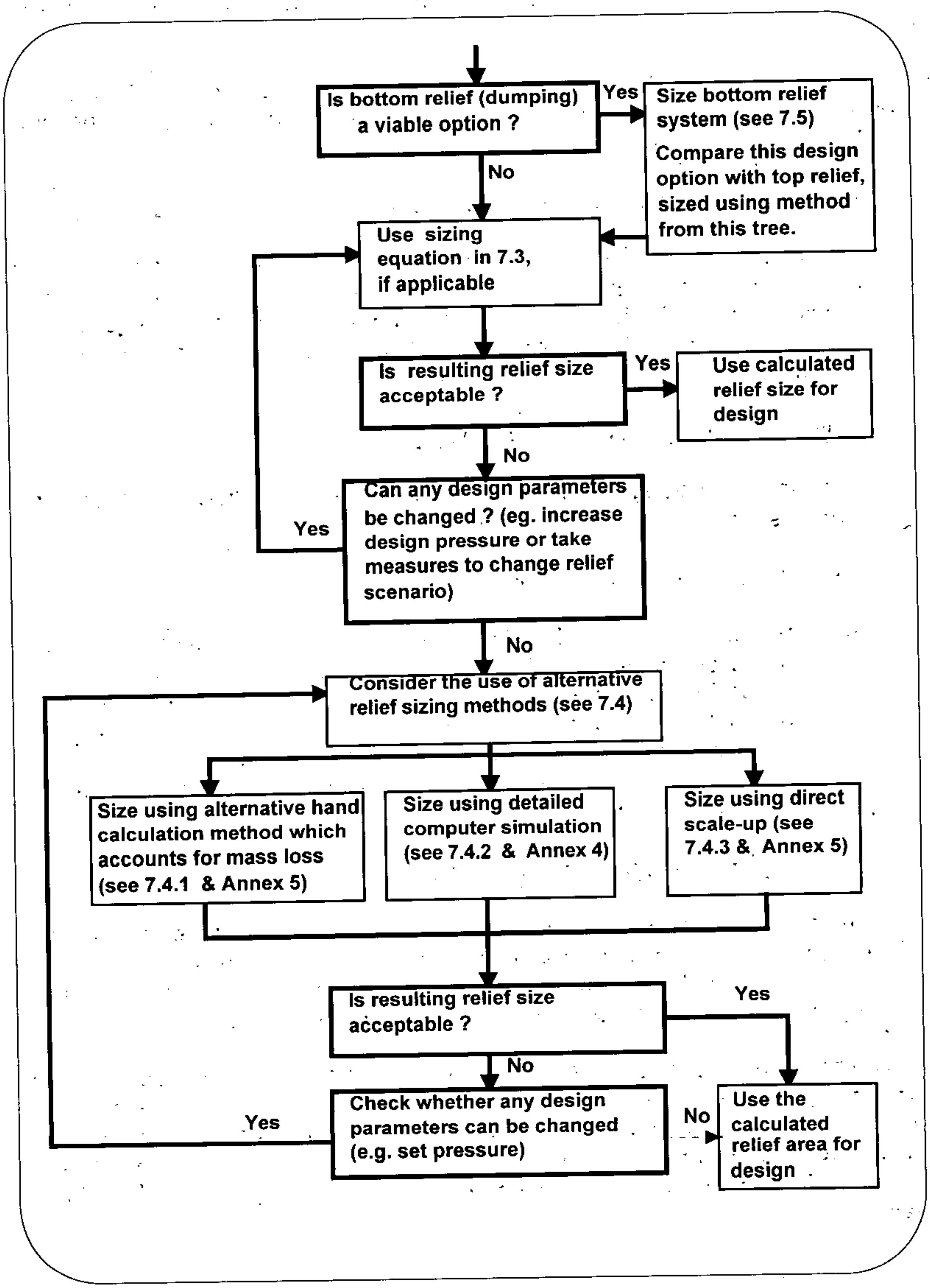
7.2 CHOICE OF RELIEF PRESSURE AND TYPE OF RELIEF DEVICE

It is important to realise that, for an untempered system, the reaction rate depends primarily on the temperature and NOT on the pressure. There is no simple relationship between pressure and temperature for an untempered system during relief.

The following considerations are relevant to the selection of the relief pressure:

a) A low relief temperature means a low reaction rate when the relief system first operates, and this may allow a smaller relief system to be safely specified, due to the increased venting time.

Figure 7.2 STRATEGY FOR RELIEF SYSTEM SIZING FOR GASSY SYSTEMS



b) It is desirable to arrange for the reactor to empty via the relief system as much as possible and as fast as possible. This will reduce the effects of the very high reaction rate at the peak temperature attained by an untempered reaction.

In order to optimise the above, for any situation, it is necessary to consider the type of relief system and the presence or otherwise of any process vents. The variables within this optimisation process are:

i) <u>Relief from the top or the bottom of the reactor</u>

Relief from the bottom of the reactor is likely to maximise the rate of emptying of the reactor compared with relief from the top. However, if a top relief system (particularly via a bursting disc) or a process vent is also required, the pressure in the reactor is likely to be reduced and impair the efficiency of bottom relief.

ii) <u>Relief via a bursting disc or a safety valve</u>

The use of a bursting disc, rather than a safety valve, is likely to maximise the mass loss from the reactor. This is because:

(a) It is always open after bursting.

(b) Gas dissolved in the liquid under pressure may be released on sudden depressurisation (the champagne bottle effect). A bursting disc can cause more depressurisation than a safety valve that reseats when the pressure starts to fall. (It is unlikely that this effect of dissolved gas could be sufficiently well modelled to take account of it during relief sizing, except by using direct scale-up, or possibly computer simulation, to find the relief size.)

iii) <u>The presence or absence of a process vent</u>

Process vents should be avoided if at all possible, or at least restricted to the minimum necessary diameter. A process vent will act to slow the rate of pressure rise to the relief pressure, so that the relief pressure coincides with a higher temperature and correspondingly higher reaction rate.

In spite of the above qualitative reasons for preferring a low relief temperature, the simple sizing equation (see 7.3 below) for gassy systems does not enable any benefit (in terms of a reduced relief size) to be obtained from either a low relief temperature or a low relief pressure. Alternative relief sizing methods (see 7.4) do allow such factors to be taken into account and for a smaller relief size to be obtained.

7.3 SIZING METHOD FOR TOP VENTING OF GASSY SYSTEMS

The following sizing equation[1] assumes:

a) relief from the top of the reactor;

b) the reaction rate is the peak rate for the reaction;

c) all of the reacting mixture remains in the reactor until the peak rate of gas evolution is reached (this is conservative);

d) homogeneous two-phase relief occurs at the peak rate of gas generation (this is conservative when assumed together with (c) above);

e) the relief system is to be sized to hold the pressure constant, rather than taking any account of emptying during a permitted overpressure;

f) there is no heat gain or heat loss from the reactor contents. (It is safe to use the method if the contents of the real reactor are subject to heat loss; in the case of heat gain (from process heating or external fire), the method will be safe if the peak rate of gas evolution was measured in a test which simulated the heat input);

g) apart from the relief stream, the reactor is a closed vessel. Thus, the rate of any continuing feed stream is assumed to be negligible.

The combination of these assumptions should usually be conservative, because no account is taken of material removed from the reactor by the relief system before the peak gas generation rate is reached.

The sizing method is:

$$W = Q_{G\max} \frac{m_R}{V} \tag{7.1}$$

The peak gas evolution rate, Q_{Gmax}, can be obtained from calorimetric measurements (see Annex 2 and equations (A2.3) and (A2.4)). It is important that such calorimetric tests are performed so as to minimise the amount of dissolved gas in the test. "Open" tests are therefore preferred to "closed" tests[2].

The required relief flow area, A, can be obtained from the required relief rate, W, given in equation (7.1) using equation (5.1):

$$A = \frac{W}{G} \tag{5.1}$$

The two-phase mass flow capacity per unit cross-sectional area, G, can be calculated using any applicable method for non-flashing two-phase flow (see Chapter 9). In order to minimise the relief size obtained, G should be evaluated at the maximum accumulated pressure, irrespective of the relief pressure.

7.4 ALTERNATIVE RELIEF SYSTEM SIZING METHODS FOR TOP VENTING OF GASSY SYSTEMS

7.4.1 Hand calculation methods which account for mass loss

Equation (7.1) takes no account of any mass loss through the relief system before the peak reaction rate is reached. This is approximately true in the case where gas-only venting occurs right until the peak rate. It could be expected to be very conservative in cases where homogeneous two-phase relief occurred, for example due to inherent foaminess of the reacting mixture (see Annex 3).

Singh[3] and Leung[4] have both derived sizing methods that assume a homogeneous two-phase mixture is present in the reactor and enters the relief system. However, this is a potentially non-conservative assumption. It is recommended that, unless it is known that homogeneous flow occurs during relief, this should be checked experimentally before these methods are used (see A2.3.2). Full details of the methods and their conditions of applicability are given in A5.9 and A5.10. The two methods make different assumptions in their derivations and so it will depend on the particular application which method gives the smaller relief size.

7.4.2 Detailed computer simulation

Information about computer simulation methods is given in Annex 4.

It is important that the computer code chosen is suitable for carrying out physical property calculations for pure gassy systems. Most simulation codes require the reaction mechanism to be sufficiently well understood that data including stoichiometric coefficients for the reaction and the molecular weight of the evolved gas(es) can be supplied. It is recommended that these data be derived from suitable adiabatic experiments (see Annex 2). A few codes make direct use of adiabatic experimental data, so that a full understanding of the reaction is not required. Most codes assume that the evolved gas can be treated as ideal, and, if this is not the case, an appropriate code must be found.

For gassy systems, computer simulation has the advantage that level swell can be simulated and account can be taken of two-phase venting that contains a higher fraction of gas than the average for the vessel (giving rise to a lower rate of mass loss than for homogeneous relief). This allows a more accurate and smaller relief size to be found than is obtained using equation (7.1). It is important to check that the code chosen carries out rigorous calculation of the gas fraction entering the relief system, e.g. using the DIERS coupling equation (see A3.4). (However, such calculations will not be accurate if the actual flow regime is not one of those modelled by the code. This could be a particular problem if the gas evolution rate is so high that a gas-continuous flow regime exists.) It is recommended that the sensitivity of the relief size to the level swell assumptions be carefully checked, and that a suitable safety factor is applied to the calculated relief size (see Annex 7).

7.4.3 Direct scale-up

Direct scale-up may be used to obtain a relief system size that is less conservative than the DIERS equation. Direct scale-up and its many conditions of applicability are detailed in A5.12. A direct scale-up test is only applicable if the test reactor empties totally by two-phase relief[6], and the applicability of the method can therefore only be assessed after the scale-up test has been performed. Direct scale-up may not be feasible if the reacting system contains solids with a particle size similar to or larger than the diameter of the small-scale relief system.

7.5 SIZING METHODS FOR BOTTOM RELIEF (DUMPING) OF GASSY REACTIONS

The Boyle method (see A5.13) can be used to estimate the diameter required for a dump system. It will usually be safe to assume liquid-only flow if dumping occurs well before the maximum rate (the original Boyle method). Alternatively, the conservative assumption that a homogeneous two-phase mixture (rather than liquid alone) enters the dump system from the reactor could be made (the modified Boyle method).

Many computer simulation codes (see Annex 4 and 7.4.2) allow the option of specifying a bottom relief system. This can be particularly useful if the effects of simultaneous venting from the top of the reactor needs to be assessed, provided that the code selected contains this option. Again, it will usually be safe to assume liquid only flow if dumping occurs well before the maximum rate..

7.6 WORKED EXAMPLE OF RELIEF SYSTEM SIZING FOR A GASSY RUNAWAY REACTION

A reactor of volume 3.5 m^3 has a design pressure of 14 barg. A worst case relief scenario has been identified in which a gassy decomposition reaction occurs. The mass of reactants in the reactor would be 2500 kg. An open cell test has been performed in a DIERS bench-scale apparatus, in which the volume of the gas space in the apparatus was 3,800 ml, and the mass of the sample was 44.8 g. The peak rate of pressure rise was 2,263 N/m^2s at a temperature of 246°C, and the corresponding rate of temperature rise was 144°C/minute. (These values include corrections for thermal inertia.) The pressure in the containment vessel corresponding to the peak rate was 20.2 bara.

The liquid density at 246°C is estimated as 820 kg/m^3. The gas generated by the runaway has a C_p/C_v value of 1.3.

The problem is to evaluate the relief size required. Relief is to be via a bursting disc system with an overall length of 12 metres and two 90° bends with a velocity head loss of 0.2 per bend. The bursting disc has an equivalent length to diameter ratio of 20.

The peak rate of gas evolution in the reactor can be calculated using an equation from Annex 2:

$$Q_G = \frac{V_e}{P}\left(\frac{dP}{dt}\right)_e \frac{T_e'}{T_c}\frac{m}{m_e} \qquad \text{(A2.4)}$$

V_e is the volume of the gas space in the containment vessel, and T_c is the containment vessel temperature. An average has been taken between ambient (20°C) and the maximum test cell temperature of 246°C, i.e. a value of 133°C. The calculation is carried out at the maximum accumulated pressure. Thus:

$$Q_G = \frac{3800x10^{-6}}{(14x1.1+1)x10^5} x2263x\frac{(246+273)}{(133+273)}x\frac{2500}{44.8x10^{-3}} = 0.374 \quad m^3/s$$

The required relief rate can now be calculated:

$$W = Q_{G_{max}}\frac{m_R}{V} \qquad (7.1)$$

$$W = 0.374\ x\ \frac{2500}{3.5} = 267.1 \quad kg/s$$

In order to find the relief area, it is necessary to calculate G. This will be done using Tangren et al.'s method for frictionless flow, and correcting for the effects of friction using the Omega method.

The void fraction at the inlet to the relief system will be estimated assuming the reactor contains a homogeneous two-phase mixture. This is consistent with the assumptions of the relief sizing method used.

$$\alpha_0 = \frac{V-\frac{m}{\rho_f}}{V} = \frac{3.5-\frac{2500}{820}}{3.5} = 0.129 \qquad (6.8)$$

Using Tangren et al.'s method (see 9.4.3):

$$\eta_c = \left[2.016 + \left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714} = \left[2.016 + \left(\frac{1-0.129}{2x0.129}\right)^{0.7}\right]^{-0.714} = 0.3495 \qquad (9.5)$$

$$P_0\eta_c = 16.41x0.3495 = 5.74 \quad bara$$

This exceeds atmospheric pressure and so flow is choked (see equation (9.6)). The method is therefore applicable, provided that a correction is made for the effects of friction.

A frictionless G can now be calculated using Tangren et al's method, with $\eta = \eta_c = 0.3495$:

$$G = \sqrt{\frac{P}{v}}\,\frac{\left(\frac{2}{\alpha_0}\left[\left(\frac{1-\alpha_0}{\alpha_0}\right)(1-\eta)-\ln\eta\right]\right)^{0.5}}{\frac{1}{\eta}+\left(\frac{1-\alpha_0}{\alpha_0}\right)} \qquad (9.8)$$

Note that for a homogeneous two-phase mixture in the reactor, v = V/m = 3.5/2500 = 0.0014 m^3/kg.

$$G = \sqrt{\frac{16.41x10^5}{0.0014}}\,\frac{\left(\frac{2}{0.129}\left[\left[\left(\frac{1-0.129}{0.129}\right)(1-0.3495)\right]-\ln(0.3495)\right]\right)^{0.5}}{\left[\left(\frac{1}{0.3495}\right)+\left(\frac{1-0.129}{0.129}\right)\right]} = 32704\ \text{kg/m}^2\text{s}$$

This must now be corrected for the effects of friction. It is useful to have an approximate idea of the relief diameter in order to carry out the correction. Using the uncorrected value of G, A=W/G = 329.3/32704 = 0.010 m^2. The equivalent diameter is 0.113 m. The next largest standard pipe size will be 0.15 m diameter (6 inches).

The velocity head loss equivalent to the relief line can be estimated assuming a diameter of 0.15 metres.

Actual length =	12 m
Bursting disc (L/D=20)= 20 x 0.15 =	3 m
	15m

This can be converted to a velocity head loss, 4fL/D, assuming that the friction factor, 4f, is approximately equal to 0.02 for two-phase flow. It can then be added to the head loss for the two bends.

$$4f\frac{L}{D} = \left(0.02x\frac{15}{0.15}\right) + (2x0.2) = 2.4$$

For gassy systems, the Omega parameter is given by (see Annex 8):

$$\omega = \frac{\alpha_0}{k} = \frac{0.129}{1.3} = 0.099 \qquad (A8.10)$$

Figure A8.3 can now be used to obtain a friction correction factor, given ω = 0.099 and 4fL/D = 2.4. Reading from the graph gives a correction factor of 0.6.

Corrected G = 0.6 x 32704 = 19,620 kg/m^2s

The required relief area can now be calculated:

$$A = \frac{W}{G} = \frac{267.1}{19620} = 0.0136\ \text{m}^2$$

The equivalent diameter is $\sqrt{\frac{4x0.0136}{\Pi}} = 0.132$ m

The calculation has therefore converged and the required relief system diameter is 0.15 metres (the next largest standard pipe size).

REFERENCES FOR CHAPTER 7

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2. J C Etchells, T J Snee and A J Wilday, "Relief System Sizing for Exothermic Runaway : The UK HSE Strategy", International Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, 135-162, AIChE, 1998, ISBN 0-8169-0761-7

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4. J C Leung, "Venting of Runaway Reactions with Gas Generation", AIChE Journal, 723-732, Vol 38, No 5, 1992

5. A J Wilday, Jaswant Singh & K R Cliffe, "Development of a Dynamic Model for Pressure Relief of Gas Generating Chemical Reactions", IChemE Symposium Series No 141, 523 - 536, 1997

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CHAPTER 8

HYBRID SYSTEMS

8.1 STRATEGY FOR RELIEF SYSTEM SIZING

The logic given in Figure 5.1 can be used to check that this section is the correct one for relief sizing for any particular case.

The sizing method to be used for a hybrid system depends on whether that system is tempered or untempered under the relief conditions of interest. See 4.2 and Annex 2 for discussion of how to determine whether or not a system is tempered.

In general terms, tempered hybrids behave in a similar way to vapour pressure systems (see Chapter 6) and untempered hybrids behave in a similar way to gassy systems (see Chapter 7). However, many of the sizing methods developed for vapour pressure and gassy systems are inapplicable for hybrid systems because:

a) the methods for vapour pressure systems take no account of the permanent gas produced and so are non-conservative for tempered hybrid systems;

b) the methods for vapour pressure systems assume that tempering occurs and so are very non-conservative for untempered hybrid systems;

c) the methods for gassy systems take no account of tempering and so are unnecessarily conservative for tempered hybrids;

d) the methods for gassy systems take no account of the vapour generation in a hybrid system and so may be non-conservative for untempered hybrids.

Figure 8.1 can be used to select a suitable relief sizing method for a hybrid system.

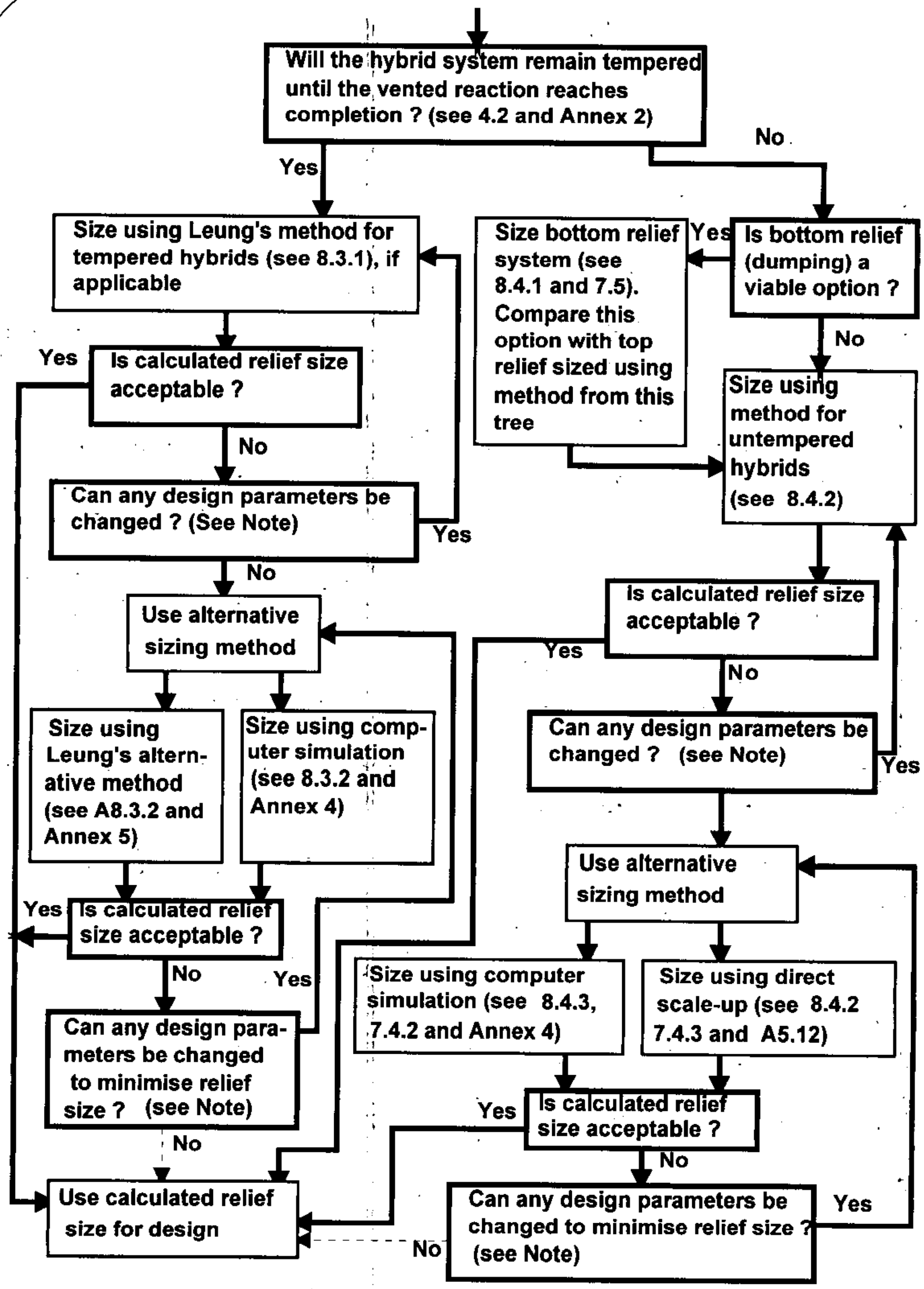
8.2 CHOICE OF SET PRESSURE AND TYPE OF RELIEF DEVICE

For both tempered and untempered hybrids, a low temperature and correspondingly low reaction rate at the relief pressure is desirable in order to reduce the relief system size.

8.2.1 Tempered hybrids

The discussion for vapour pressure systems in 6.2 also applies to tempered hybrids. A low relief pressure is beneficial because:

Figure 8.1 STRATEGY FOR RELIEF SYSTEM SIZING FOR HYBRID SYSTEMS



Note: e.g. increase design pressure, take measures to change relief scenario. Check that design changes do not alter whether or not the hybrid is tempered, e.g. increasing the maximum accumulated pressure could cause a reacting mixture to no longer temper.

a) it reduces the tempering temperature and the reaction rate during relief;

b) it allows a greater margin to be provided between the relief pressure and the maximum permitted pressure, thus providing more time for emptying of the reactor.

8.2.2 Untempered hybrids

As for gassy systems (see 7.2), the operation of the relief system cannot control the temperature or the reaction rate of untempered hybrid systems. Consequently, these will continue to rise to their peak values. However, a low relief pressure can still be beneficial because:

a) it ensures a low relief temperature and low reaction rate when the relief system first operates and this may reduce the required relief system size;

b) it allows a greater margin to be provided between the relief pressure and the maximum accumulated pressure, thus providing more time for emptying of the reactor to occur.

As for gassy systems, it may be beneficial to provide bottom relief rather than relief from the top of the reactor, and use of a bursting disc may be preferable to a safety valve.

8.3 RELIEF SYSTEM SIZING FOR TEMPERED HYBRIDS WITH TWO-PHASE FLOW

It is important that these sizing methods are only used if the hybrid is tempered and remains tempered until the reaction is complete in an open test (see 4.2 and Annex 2). If the methods in this section are used for untempered hybrid systems, the calculated relief size is likely to be inadequate.

8.3.1 Leung's method for tempered hybrids[1,2]

This is related to Leung's method for vapour pressure systems (see 6.3) and shares the same assumptions and conditions of applicability as are detailed in 6.3.1. Additionally, the method assumes the following:

a) The ratio of moles of gas to moles of vapour produced by the reaction is constant. This should be the case if there is a single reaction occurring over the temperature range of interest.

b) The temperature is allowed to rise during relief by the amount that would cause the pressure in a closed vessel to rise from the relief pressure to the maximum pressure allowed. This is a conservative assumption.

The relief size should also be calculated using Leung's method for vapour pressure systems (see 6.3) and the larger of the vapour pressure system and tempered hybrid system relief sizes should be used[2].

The sizing method for tempered hybrids[1,2] is given by:

$$W = \frac{m_R\,\bar{q}}{\left[\left(\frac{V}{m_R}\frac{h_{fg}}{v_{fg}}\frac{P_V}{P}\right)^{0.5} + \left(C_f\,\Delta T_H\right)^{0.5}\right]^2} \qquad (8.1)$$

The alternative version (obtained by using the Clausius-Clapeyron thermodynamic relationship, which only holds if the mixture behaves as a single pseudo-component) is:

$$W = \frac{m_R\,\bar{q}}{\left[\left(\frac{V\,T}{m_R}\frac{dP_V}{dT}\frac{P_V}{P}\right)^{0.5} + \left(C_f\,\Delta T_H\right)^{0.5}\right]^2} \qquad (8.2)$$

Most of the data in equations (8.1) and (8.2) are obtained as for vapour pressure systems (see section 6.3). The required relief flow area, A, can be obtained from the required relief rate, W, using equation (5.1):

$$A = \frac{W}{G} \qquad (5.1)$$

The evaluation of the two-phase mass relief capacity per unit area, G, is discussed in Chapter 9. The additional parameters which are required for tempered hybrid systems are P_v/P, the ratio of the vapour pressure to the absolute pressure, and ΔT_H, the closed vessel temperature rise as the pressure rises from the relief pressure to the maximum pressure.

P_v/P can be evaluated from the following relationship, which holds if the system is ideal, and is usually evaluated at the tempering temperature corresponding to the relief pressure:

$$\frac{P_V}{P} = \frac{Q_V}{Q_V + Q_G} \qquad (8.3)$$

Q_v and Q_G should be evaluated at the same temperature and pressure, usually the relief pressure. Q_G, the volumetric rate of gas evolution, can be obtained from measurements in a calorimetric test by the use of equations (A2.3) or (A2.4) (see Annex 2). Q_v is the volumetric rate of vapour generation and can be calculated, as follows, from the rate of temperature rise in a closed calorimetric test or in an open test with a high superimposed containment pressure (see Annex 2).

$$Q_V = \frac{m\,C_f}{\rho_V\,h_{fg}}\frac{dT}{dt} \approx \frac{m\,C_f}{T}\frac{dT}{dt}\left(\frac{dP_V}{dT}\right)^{-1} \qquad (8.4)$$

ΔT_H can be calculated by the following method:

$$\Delta T_H = \frac{(P_m - P_R)}{\left(\frac{\Delta P}{\Delta T}\right)_{closed}} \tag{8.5}$$

where:

$$\left(\frac{\Delta P}{\Delta T}\right)_{closed} = \left(\frac{dP_v}{dT}\right)_R + \frac{\left(\frac{dP_G}{dt}\right)_R}{\left(\frac{dT}{dt}\right)_R} \tag{8.6}$$

and:

$$\left(\frac{dP_G}{dt}\right)_R = \frac{P_R\, Q_{G_R}}{\alpha_R\, V} \tag{8.7}$$

$(dP_v/dT)_R$ can either be estimated from vapour pressure data (e.g. Antoine coefficients) if available or can be approximated from a knowledge of the tempering temperatures at two pressures (which will usually be the relief pressure and maximum accumulated pressure):

$$\left(\frac{dP_v}{dT}\right)_R \approx \frac{P_v}{P} \frac{(P_m - P_R)}{(T_{Tm} - T_{TR})} \tag{8.8}$$

Note that the parameters in equations (8.6), (8.7) and (8.8) should be evaluated at the tempering temperature corresponding to the relief pressure.

Alternatively, ΔT_H could be measured in a closed vessel calorimetric test, but the pressures used in the small-scale apparatus would need adjusting to account for any difference in gas volume to sample mass ratio from the full-scale reactor.

A worked example is given in 8.5.

8.3.2 Alternative relief system sizing methods for tempered hybrid systems

Leung[3,4] has proposed an alternative sizing method for tempered hybrid systems (see A5.11). This method makes the same assumptions as that above, except that the conservative assumption that the allowable temperature rise is the same as that in a closed vessel does not need to be made. The method is therefore likely to yield smaller relief sizes than the method above. However, the method is more time-consuming to evaluate as it requires a trial and error procedure.

Computer simulation can also be used for relief sizing (see Annex 4). This may be the only safe alternative in cases where physical properties are non-ideal, multiple reactions occur or there are significant continuing feed streams or external heating. It will be necessary to choose a computer simulation package which can handle multi-component mixtures comprising both volatile and permanent gas components.

It may also be possible to use computer simulation in cases where the reaction is initially tempered but stops tempering later in the runaway when a volatile solvent has boiled off. However, a good understanding of the reacting system would be required in order to have confidence in the results of such a simulation. Alternatively, the reaction could be treated as an untempered hybrid (see 8.4).

8.4 RELIEF SYSTEM SIZING FOR UNTEMPERED HYBRIDS WITH TWO-PHASE RELIEF

8.4.1 Bottom relief (dumping)

As for gassy systems, relief from the bottom of the reactor (dumping) may be a better option than relief from the top, for untempered hybrids. This is discussed in 7.5.

8.4.2 Sizing for top-venting of untempered hybrids

If top relief is to be used, DIERS proposed the following simple sizing method. This method has the same assumptions and conditions of applicability as the equation proposed for gassy systems (see section 7.3). The version for untempered hybrids is:

$$W = (Q_{G\max} + Q_{v\max})\,\frac{m_R}{V} \qquad (8.9)$$

An open system calorimetric test will tend to measure Q_{Gmax}, rather than the sum of Q_{Gmax} and Q_{vmax}, because the vapour produced will tend to condense in the relatively cold containment vessel. A closed system test will also underestimate Q_{vmax} because the high pressure will suppress vaporisation. Q_{vmax} could also be calculated from:

$$Q_{v\max} = \frac{m_R\, C_f}{h_{fg}\, \rho_v}\left(\frac{dT}{dt}\right)_{\max} \qquad (8.10)$$

However, equation (8.9) is already conservative in many cases because it neglects any mass loss which may occur before the peak reaction rate. DIERS[5] suggested that the value of Q_{Gmax} (obtained from calorimetric data using equations (A2.3) or (A2.4) of Annex 2) can be used to represent the sum of Q_{Gmax} and Q_{vmax}. This may be less reasonable if the amount of vapour produced is high, but just too low to cause tempering. This can be checked using equation (8.10), even if estimates of the physical properties (e.g. those for typical organic materials) have to be made.

The required relief flow area, A, can be calculated using equation (5.1). The two-phase mass flow capacity per unit cross-sectional area, G, can be calculated using a suitable method for hybrid systems (see Chapter 9). In order to minimise the relief size obtained, G should be evaluated at the maximum pressure permitted in the reactor during relief, irrespective of the relief pressure.

8.4.3 Alternative sizing methods for untempered hybrids

As for gassy systems, detailed computer simulation or direct scale-up (if applicable) can be used as alternative relief sizing methods for untempered hybrids. These methods are further discussed in section 7.4.

8.5 WORKED EXAMPLE OF RELIEF SYSTEM SIZING FOR A TEMPERED HYBRID RUNAWAY REACTION

(Relief sizing for untempered hybrids is similar to that for gassy systems, for which a worked example is given in section 7.6)

It is required to size a bursting disc system with a maximum specified bursting pressure of 2.2 barg (3.2 bara) for a reactor of volume 1.5 m^3 and design pressure 3 barg (maximum accumulated pressure = 4.3 bara). The frictional resistance of the bursting disc system in this case is equivalent to 4fL/D = 5. The worst case reaction has been identified as a tempered hybrid, and an open system calorimetric test has demonstrated that it will continue to temper until the reaction is complete. For the worst case reaction, the mass in the reactor would be 860 kg.

Calorimetric testing has produced the following data:

At the relief pressure of 3.2 bara

> tempering temperature = 80°C = 353 K
> adiabatic rate of temperature rise = 20 °C/minute
> volumetric rate of gas generation, Q_G (calculated from the rate of pressure rise in an open system test using equation A2.4) = 0.0279 m^3/s

At the maximum accumulated pressure of 4.3 bara

> tempering temperature = 96°C = 369 K
> adiabatic rate of temperature rise = 35 °C/minute

The above calorimetric data have been corrected for the effects of the thermal inertia, ϕ (see A2.7.2).

A value of G has been calculated using the Omega method. This is shown as a worked example in A8.5 and G is calculated as 3792 kg/m^2s at the relief pressure of 3.2 bara.

The following physical property data have been compiled:

Pressure (bara)	3.2	4.3	average
Temperature (K)	353	369	
Liquid density (kg/m^3)	820	809	
Vapour density (kg/m^3)	8.18	10.5	
v_{fg} (m^3/kg)	0.12	0.09	0.105
Latent heat (kJ/kg)	621	604	612.5
Liquid specific heat (kJ/kgK)	1.98	2.07	2.03

In addition, isentropic coefficients are estimated as 1.05 for the vapour and 1.2 for the gas.

The required relief rate will be calculated using Leung's method for tempered hybrids:

$$W = \frac{m_R\,\bar{q}}{\left[\left(\frac{V}{m_R}\frac{T}{}\frac{dP_V}{dT}\frac{P_V}{P}\right)^{0.5} + \left(C_f\ \Delta T_H\right)^{0.5}\right]^2} \qquad (8.2)$$

Calculation of average q

The absolute overpressure is only 35%, so it is reasonable to use equation (6.2) to find the average value of q.

$$\bar{q} = 0.5\ C_f\left[\left(\frac{dT}{dt}\right)_R + \left(\frac{dT}{dt}\right)_m\right] \qquad (6.2)$$

$$\bar{q} = 0.5x2030x\left[\frac{20}{60} + \frac{35}{60}\right] = 930.4\ W/kg$$

Calculation of P_V/P

Using equation (8.4) at the relief pressure:

$$Q_V = \frac{m}{\rho_V}\frac{C_f}{h_{fg}}\frac{dT}{dt} = \frac{860}{8.18}x\frac{1980}{621000}x\frac{20}{60} = 0.1117\ m^3/s$$

Q_G at the relief pressure is given as 0.0279 m^3/s, so, using equation (8.3):

$$\frac{P_V}{P} = \frac{Q_V}{Q_V+Q_G} = \frac{0.1117}{0.1117+0.0279} = 0.800$$

Calculate ΔT_H

The void fraction at the relief pressure is given by:

$$\alpha = \frac{\left(V - \frac{m_R}{\rho_f}\right)}{V} = \frac{1.5 - \left(\frac{860}{820}\right)}{1.5} = 0.3008 \qquad (6.8)$$

Using equation (8.7):

$$\left(\frac{dP_G}{dt}\right)_R = \frac{P_R\, Q_{GR}}{\alpha_R\, V} = \frac{3.2\text{x}10^5 \text{ x } 0.0279}{0.3008 \text{ x } 1.5} = 19787\ N/m^2s$$

Using equation (8.8):

$$\left(\frac{dP_v}{dT}\right)_R \approx \frac{P_v}{P}\frac{(P_m - P_R)}{(T_{Tm} - T_{TR})} = 0.8\frac{\left(4.3\text{x}10^5 - 3.2\text{x}10^5\right)}{(369-353)} = 5500\ N/m^2K$$

Using equation (8.6):

$$\left(\frac{\Delta P}{\Delta T}\right)_{closed} = \left(\frac{dP_v}{dT}\right)_R + \frac{\left(\frac{dP_G}{dt}\right)_R}{\left(\frac{dT}{dt}\right)_R} = 5500 + \frac{19787}{(20/60)} = 64861\ N/m^2K$$

Using equation (8.5):

$$\Delta T_H = \frac{(P_m - P_R)}{\left(\frac{\Delta P}{\Delta T}\right)_{closed}} = \frac{(4.3 - 3.2)\text{x}10^5}{64861} = 1.70\ K$$

Calculate relief size required

Using Leung's method for tempered hybrids, equation (8.1):

$$W = \frac{m_R\, \bar{q}}{\left[\left(\frac{V}{m_R}\frac{h_{fg}}{v_{fg}}\frac{P_v}{P}\right)^{0.5} + \left(C_f\, \Delta T_H\right)^{0.5}\right]^2}$$

$$W = \frac{860 \text{ x } 930.4}{\left[\left(\frac{1.5}{860}\text{x}\frac{612500}{0.105}\text{x } 0.800\right)^{0.5} + (2030 \text{ x } 1.7)^{0.5}\right]^2} = 36.1\ kg/s$$

Relief system size

For a the hybrid system, G is estimated as 3792 kg/m^2s at the relief pressure of 3.2 bara. It is permissible to use an average value of G between the relief pressure and the maximum permitted pressure. An average value of G can be estimated:

$$G = G_R\left(1 + 0.5\left(\frac{P_m - P_R}{P_R}\right)\right) = 3792\left(1 + 0.5\left(\frac{4.3-3.2}{3.2}\right)\right) = 4444\ kg/m^2s \qquad (6.7)$$

This can now be used to find the required relief area

$$A = \frac{W}{G} = \frac{36.1}{4444} = 0.00812\ m^2 \qquad (5.1)$$

The equivalent diameter of the bursting disc system is:

$$D = \sqrt{\frac{4A}{\Pi}} = 0.102\ m$$

Check required relief size for vapour pressure system

The relief system must also be sized assuming the tempered hybrid is a vapour pressure system, and the larger relief diameter taken.

Using equation (6.5):

$$W = \frac{m_R\ \bar{q}}{\left[\left(\frac{V}{m_R}\frac{h_{fg}}{v_{fg}}\right)^{0.5} + \left(C_f\ \Delta T\right)^{0.5}\right]^2}$$

$$W = \frac{860\ x\ 930.4}{\left[\left(\frac{1.5}{860} x \frac{612500}{0.105}\right)^{0.5} + (2030\ x\ 16)^{0.5}\right]^2} = 10.1\ kg/s$$

In this case, G is estimated as 2990 kg/m^{2}s using the Omega method (calculation not shown).

$$A = \frac{W}{G} = \frac{10.1}{2990} = 0.00339\ m^2$$

Final relief size

The larger relief size is that obtained using the method for tempered hybrids, of 0.00812 m^2 and this should be used for design.

REFERENCES FOR CHAPTER 8

1. J C Leung & H K Fauske, "Runaway System Characterisation and Vent Sizing Based On DIERS Technology", Plant/Operations Prog, 6 (2), 77-83, April 1987

2. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Appendix VI-A7 (Leung Analytical Method II), DIERS/AIChE, 1992, ISBN 0-8169-0568-1

3. J C Leung, "Simplified Vent Sizing Methods Incorporating Two-Phase Flow", International Symposium on Runaway Reactions and Pressure Relief Design, 200-236, AIChE, 1995, ISBN 8169-0676-9

4. J C Leung, "Venting of Runaway Reactions With Gas Generation", AIChE Journal, Vol 38 (5), 723-732, 1992

5. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Appendix VI-A7 (Leung Analytical Method III), DIERS/AIChE, 1992, ISBN 0-8169-0568-1

CHAPTER 9

CALCULATION OF TWO-PHASE FLOW CAPACITY (G)

9.1 INTRODUCTION

The relief sizing methods detailed in Chapters 6-8 (and most methods in Annexes 4 and 5) yield an average two-phase required relief rate, W. In order to calculate the required relief flow area, A, using equation (5.1), the two-phase mass flow capacity per unit cross-sectional area of the relief system, G, is needed. This Chapter is concerned with methods for the calculation of G.

The Chapter begins by giving background information about two-phase flow in sections 9.2 and 9.3. Details of the main flow models used to calculate G are given in 9.4. The selection of methods for two-phase flow calculations for each of the system types for relief sizing (vapour pressure, gassy and hybrid: see 4.2) is discussed in 9.5. The types of calculation required for bursting disc systems and safety valve systems are then discussed in 9.6 and 9.7 respectively. A flowchart for the use of this Chapter is given in Figure 9.1.

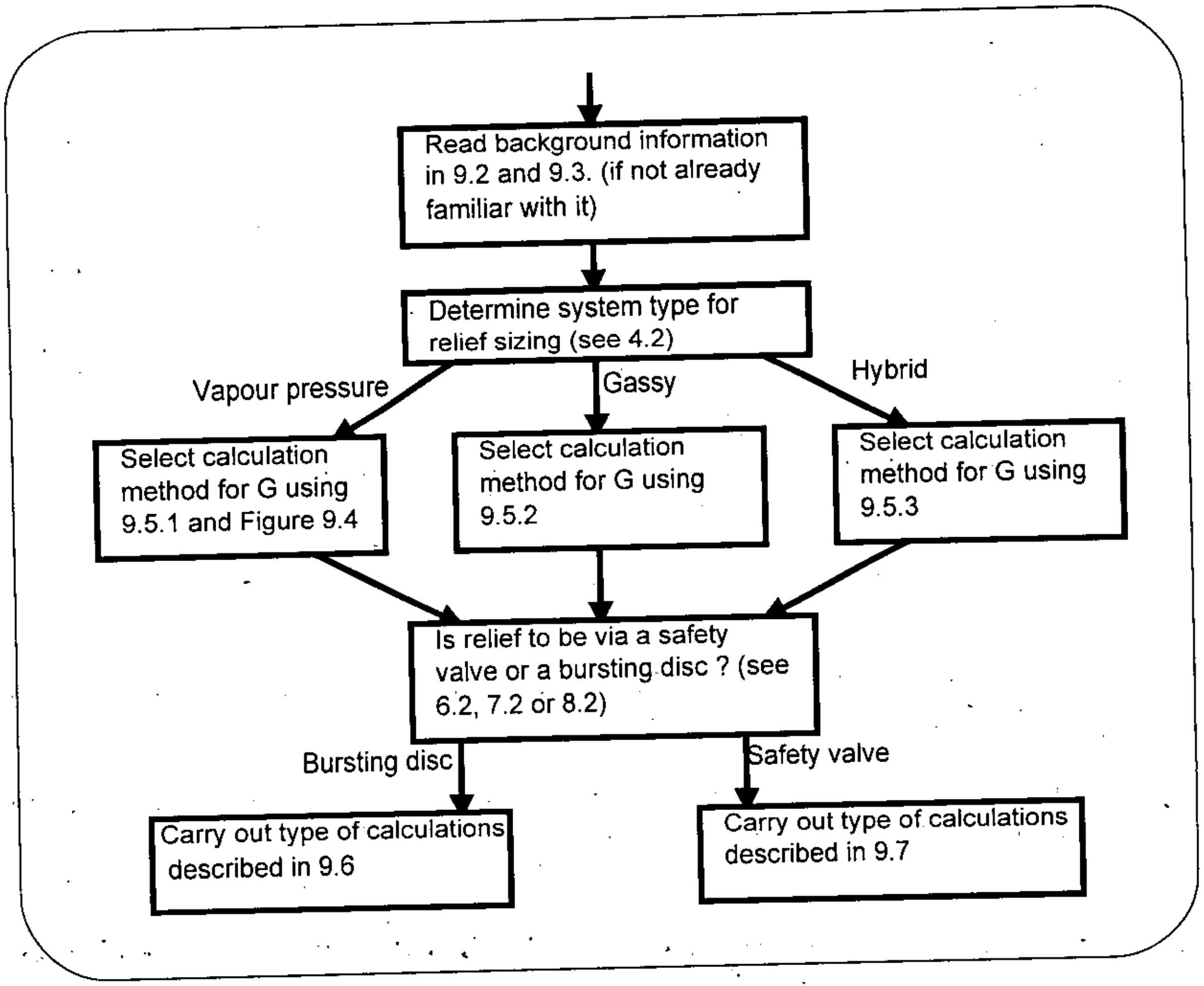
The capacity of a pressure relief system depends on its design and layout. It is recommended that relief systems are designed to be as short and as straight as practicable, with the minimum number of constrictions. This will minimise the required relief system diameter as well as simplifying the calculation of G.

9.2 THE PHENOMENON OF CHOKING IN COMPRESSIBLE FLOW

Choking is a phenomenon that occurs in high speed compressible flow (e.g. in relief systems). It occurs because, as the pressure falls along a pipe or through a nozzle, the fluid density decreases. This means that the volumetric flow rate and, hence, the velocity increases (because the mass flow is constant). Choking occurs when the downstream pressure is reduced to the point where the velocity cannot increase any more. This effectively limits the maximum velocity and, hence, flow rate of the fluid.

Two-phase flow (like gas flow) is compressible in that the fluid density varies with pressure. It is likely that during emergency relief venting the flow will be sufficiently high to choke, and many of the hand calculation methods for two-phase flow assume this (e.g. the ERM in 9.4.2 and Tangren et. al.'s method in 9.4.3). However, if the available pressure drop in the relief line is insufficient to cause choking, the relief flow rate will be overestimated (which is unsafe for design) by such methods. It is therefore important to check whether choking is expected for a given situation.

Figure 9.1 FLOW CHART FOR CALCULATION OF G

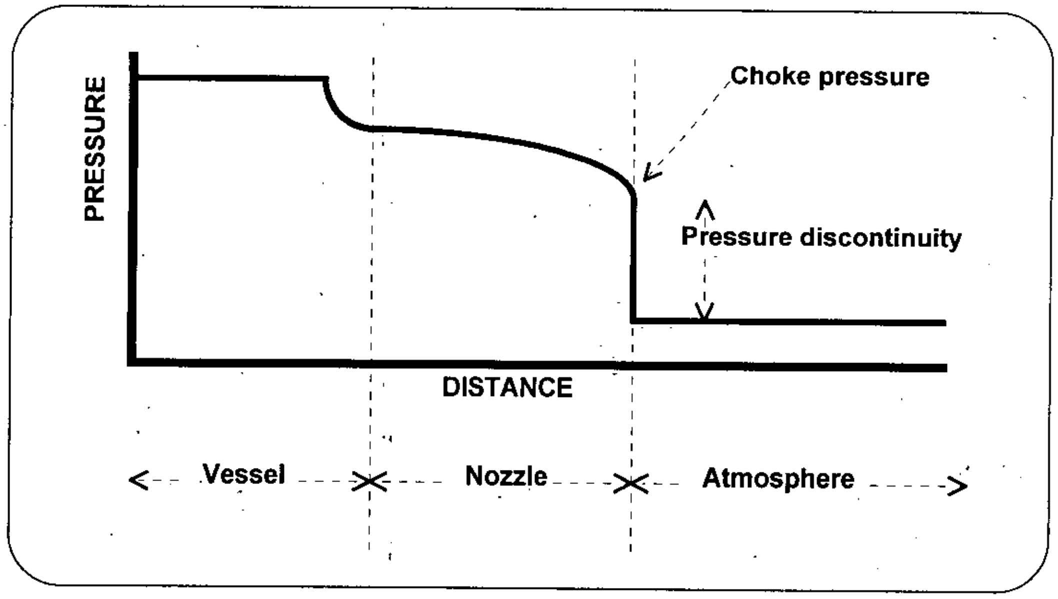


In flow through a frictionless nozzle, there is a critical pressure ratio, η, which will just cause choking. The critical pressure ratio is the ratio of the downstream back pressure to the upstream pressure, both in absolute pressure units. If the actual back pressure (e.g. atmospheric) is less than the critical pressure at which choking occurs, then there will be a pressure discontinuity at the end of the nozzle: the pressure just inside the nozzle will be the critical pressure for choking, and that just outside the nozzle will be the actual back pressure, which is normally atmospheric. See Figure 9.2.

Two-phase flow models allow the calculation of both the two-phase mass flow rate per unit area (G) and also the critical pressure for choking. DIERS recommend the homogeneous equilibrium model (HEM, see 9.4.1) for this calculation.

In relief systems of uniform diameter, the choke point (if choking occurs) will be at the downstream end of the pipe. However, if the relief system comprises more than one diameter, then multiple choke points are possible and it will be necessary to determine the position of the choke point that limits the flow. This can be a complex calculation, for which there are two common cases:

Figure 9.2 CHOKING IN A FRICTIONLESS NOZZLE



a) For safety valve systems, the flow-limiting choke is always in the safety valve nozzle. See 9.7.1.

b) Bursting disc systems with multiple diameters require iterative calculations to find the position of the flow limiting choke. See 9.6.3 and A8.4.5.

9.3 BACKGROUND INFORMATION ON THE CHOICE OF TWO-PHASE FLOW MODEL FOR RELIEF SIZING

9.3.1 Possible model assumptions for two-phase flow in relief systems

A large number of different two-phase flow models have been proposed for different purposes[1,2]. When deciding on a two-phase flow model to calculate G, choices have to be made about the following parameters:

a) Flashing or non-flashing flow. Two-phase flow may be flashing, non-flashing or a combination depending on the system type for relief sizing (vapour pressure, gassy or hybrid respectively). This is discussed in 4.2.

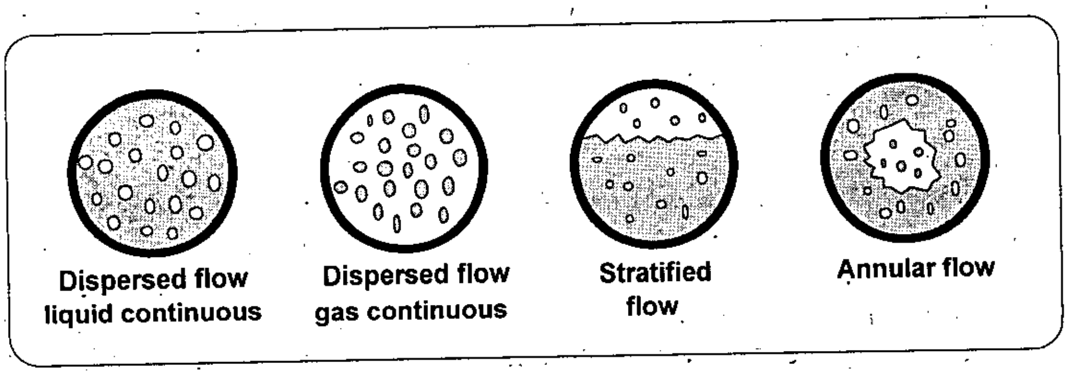
b) Flow regime. A number of flow regimes are possible for two-phase flow in relief lines, and some of them are illustrated in Figure 9.3. For the two-phase mixtures relieved from a reactor, a flow regime is likely in which the pipe is full of a two-phase mixture which is liquid continuous. This could change at the downstream end of relief lines when considerable flashing can be expected.

c) Phase slip. The vapour/ gas phase tends to travel faster along a pipe than the liquid phase. A number of possible slip flow models take account of this. No slip between the phases is a requirement of homogenous flow. The no-slip condition is sometimes also called "mechanical equilibrium".

d) Equilibrium or non-equilibrium flow. For flashing flow, a drop in pressure requires the liquid to flash in order to maintain vapour/ liquid equilibrium at the new pressure. However, flashing is a dynamic process which requires the stages of bubble nucleation and bubble growth and so takes a finite time to occur. If the path length (and consequently the residence time within the pipe) is short enough, the fluid has passed the restriction before it begins to flash. This is known as non-equilibrium flow. A path length of 0.1 metres has been shown by a number of different workers to be required to allow flashing to reach equilibrium if saturated liquid enters the short pipe[1]. However, more recent work by Richardson and Saville[3] suggests that if a two-phase mixture enters an orifice (effectively zero length) then flashing to equilibrium occurs. If non-equilibrium flow occurs, a higher flow rate than for equilibrium flashing flow will occur. Different models assume equilibrium or different degrees of non-equilibrium (see 9.3.2 below).

e) Turbulent or laminar flow. Laminar flow is discussed further in Chapter 10.

Figure 9.3 **SOME POSSIBLE FLOW REGIMES FOR RELIEF LINE TWO-PHASE FLOW**



9.3.2 Overview of possible two-phase flow models

Some possible models are as follows:

a) The Homogeneous Equilibrium Model (HEM) is recommended by DIERS[1] for relief system sizing. It is applicable to both flashing and non-flashing two-phase flow, assumes uniform mixing of the phases across the pipe diameter, no phase slip (mechanical equilibrium) and complete vapour/ liquid equilibrium. It is described in detail in 9.4.1 below.

b) The Homogeneous Frozen Model (HFM)[1] is equivalent to the HEM for a two-phase flow comprising a non-volatile liquid and a non-soluble gas and is the method recommended by DIERS for relief sizing for gassy systems. If the

HFM is applied to a system in which the liquid is volatile, then it assumes a high degree of non-equilibrium since the model does not account for any flashing and the flow could be greatly overestimated. The model is therefore not recommended for relief sizing for tempered systems.

c) The Slip Equilibrium Model[1] is applicable to both flashing and non-flashing two-phase flow, assumes uniform mixing of the phases across the pipe diameter, phase slip (mechanical non-equilibrium) and complete vapour/ liquid equilibrium. There are many possible models for the degree of slip between the phases. Slip flow models may be more conservative (lower flow) than the HEM in cases where much of the flow is vertically upwards, e.g. if the upwards static head change exceeds 10% of the upstream pressure.

d) The Omega method[4] is a simplified method of evaluating the HEM or the HFM (see above). It introduces a number of simplifying assumptions but is convenient when applicable because it does not require a computer code for its evaluation. It is described in detail in Annex 8.

e) The simplified Equilibrium Rate Model (ERM)[5] yields similar results to the HEM (approximately 10% higher flow rates) when applicable. Its use can often be quicker and more convenient than the HEM. It is applicable only to flashing two-phase flow (vapour pressure systems), assumes uniform mixing of the phases across the pipe diameter, no phase slip (mechanical equilibrium) and some limited vapour/ liquid non-equilibrium. The method assumes choking and neglects friction but a simple correction factor can be applied for friction. The ERM is described in detail in 9.4.2.

f) Tangren et al.'s method[6] is an implementation of the HFM and yields similar results (slightly lower) than the HEM. It can be quicker and more convenient to use when applicable. It is applicable only to non-flashing two-phase flow (gassy systems), assumes uniform mixing of the phases across the pipe diameter, no phase slip (mechanical equilibrium) and thermal equilibrium between the phases. The method assumes choking and neglects friction. It is described in detail in 9.4.3.

g) A method of calculating a two-phase flow rate through relief systems was given by API RP 521[7] (third edition and earlier). This method calculated a relief area for liquid and one for gas/ vapour and added them together. It is not recommended for relief system sizing and has been removed from the 1997 edition of the standard[7].

9.3.3 Conditions at inlet to the relief system

The conditions at the inlet to the relief system, i.e. the assumed upstream conditions for the flow calculation, affect the calculated flow. It is therefore important to have both an appropriate flow model and appropriate assumptions about the upstream conditions:

When calculating G, the pressure in the reactor at which the calculation is required will be known (see Chapter 5). The corresponding temperature and composition will be needed to evaluate physical properties.

One of the most significant parameters describing the inlet condition is the phase split at this position. This can be described by either the mass fraction of gas/ vapour, x, or the volume (void) fraction, α. These two parameters are related:

$$x = \frac{\alpha\rho_g}{\alpha\rho_g + (1-\alpha)\rho_f} \qquad (9.1)$$

$$\alpha = \frac{\frac{x}{\rho_g}}{\left(\frac{x}{\rho_g}\right) + \left(\frac{(1-x)}{\rho_f}\right)} \qquad (9.2)$$

The value of x or α will depend on the assumptions made about the flow regime in the venting reactor. Different relief sizing methods make different assumptions. Possible reactor flow regimes are (see Chapter 4):

a) Homogeneous, where the void fraction entering the vent is the same as the average for the vessel.

b) Churn-turbulent, where the void fraction entering the vent is greater than the average for the vessel.

c) Bubbly, where the void fraction entering the vent is greater than the average for the vessel.

Unless otherwise stated, the relief sizing methods given in this Workbook assume that the flow regime in the reactor is homogeneous ((a) above).

9.4 TWO-PHASE FLOW MODELS

9.4.1 Homogeneous equilibrium model (HEM)

The Homogeneous Equilibrium Model (HEM) assumes uniform mixing of the phases across the pipe diameter, no phase slip (mechanical equilibrium), thermal equilibrium between the phases and complete vapour/ liquid equilibrium. "Homogenous" in the context of the HEM refers to the flow in the vent line.

DIERS[1] recommend the use of the HEM for relief sizing purposes, because:

a) it gave the best fit to the DIERS experimental results;

b) it gives the lowest mass flow rate compared with other two-phase flow models (i.e. it is safest for relief sizing of tempered systems in comparison with other models for tempered systems, and for untempered systems if the methods given in Chapters 7 and 8 are used for relief sizing).

The term "HEM" simply refers to a set of assumptions, as described above, and it can be evaluated by a range of calculation procedures, sometimes introducing further assumptions. Most of the calculation procedures require a computer, and this is discussed further in Annex 4. The Omega method[4] uses a simplified "equation of state" for the fluid to estimate its specific volume at any pressure, and this allows analytical solution of the HEM. The Omega method, if applicable, can therefore be used to obtain G by reading from a graph or performing a hand calculation. Conditions of applicability, calculation methods and graphs for the Omega method are given in Annex 8.

The HEM method will tend, if anything, to underestimate the relief flow capacity and so to oversize relief systems. This is provided the upstream conditions have been correctly specified (see 9.3.3). Another possible exception to the HEM tending to underestimate flow is when there is a large upwards static head change (equivalent to greater than about 10% of the pressure in the reactor), in which case a slip flow model could be more conservative.

Care should be taken when using the HEM to size downstream disposal equipment. It may result in the flow rate being underestimated and the disposal system being undersized. It may be better to use a slip flow model in such cases. An alternative approach would be the application of an appropriate safety factor to a flow rate calculated using the HEM (see A7.2 (b)).

Although the HEM was found by DIERS[1] to be accurate for estimating G, it is much less accurate in estimating the corresponding critical pressure for choking. For example, for flow of flashing liquid through short pipes with little friction, the HEM would predict a critical pressure ratio (absolute choke pressure divided by absolute upstream vessel pressure) of about 0.9, whereas a slip flow model (which would be closer to actual fluid behaviour)[8] would suggest a critical pressure ratio closer to 0.5.

This matters most when designing a disposal system, when it is important that the back pressure exerted by flow through the disposal system does not reduce G. It may be prudent to ensure that the back pressure is at least less than 50% of the upstream reactor pressure to ensure that choking in the relief system is maintained. For safety valve systems, lower back pressures may be necessary, even for balanced valves, see 9.7.3.

9.4.2 Simplified Equilibrium Rate Model (ERM)

The ERM[5] assumes no flashing in the relief system until the choke point is reached, and flashing at equilibrium rate at the point of choking. See Figure 9.3 which distinguishes between the assumptions of the ERM and HEM for the case in which saturated liquid is relieved. The simplified ERM assumes that saturated liquid rather than a two-phase mixture enters the relief system. It tends to yield values of G which are around 10% higher than those obtained from the HEM and therefore its use, when applicable, introduces minimal inaccuracy into the calculation.

The simplified ERM makes the following assumptions:

a) The system is a vapour pressure system (see 4.2).

b) Turbulent, frictionless choked flow through a nozzle.

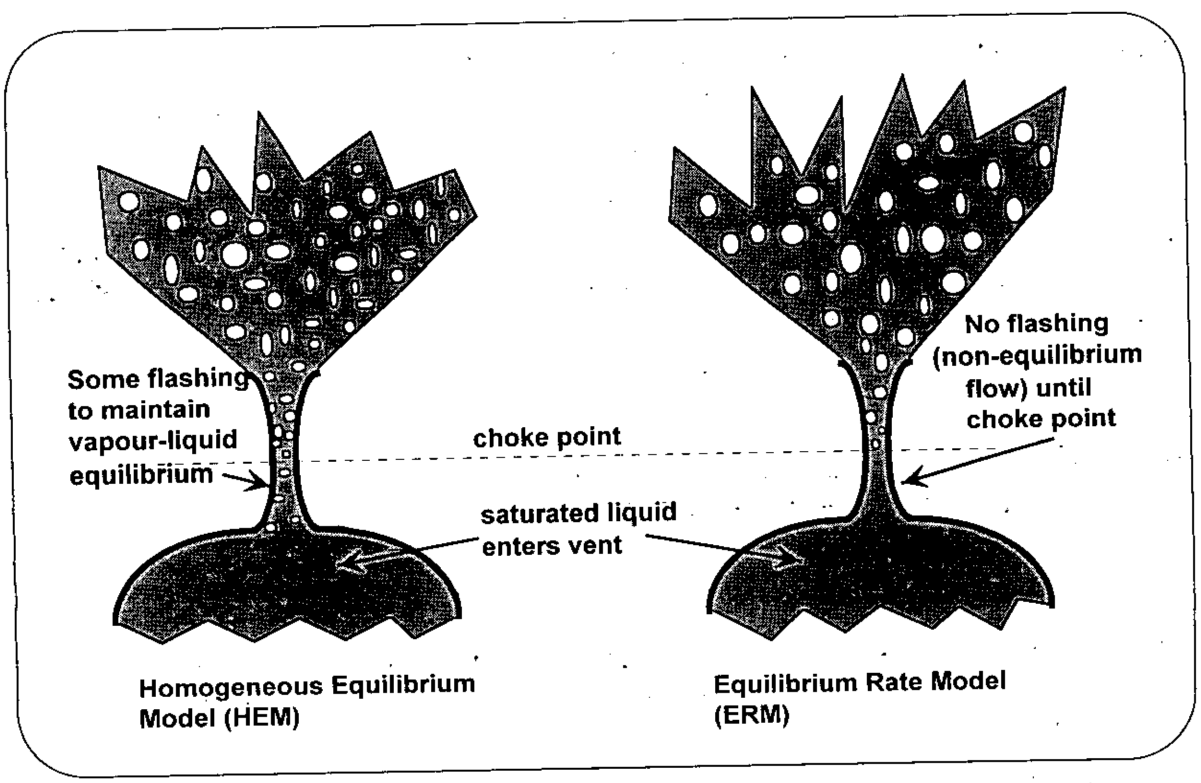
c) The path length through the nozzle is long enough (>0.1 m, see 9.3.1 (d)) to give sufficient flashing that vapour/ liquid equilibrium is maintained in the flow. The method is safe for relief sizing if this is not the case.

d) There is no slip between the liquid and vapour phases (i.e. homogeneous flow). Note that although there actually will be phase slip, both the ERM and HEM ignore it and this is usually conservative.

e) The fluid at the inlet to the relief system is a saturated liquid. The calculated value of G, using either the HEM or the ERM is reasonably insensitive to the inlet vapour fraction, but the method should be limited to inlet vapour qualities less than 0.02[9].

f) The vapour phase is an ideal gas.

Figure 9.3 COMPARISON OF ASSUMPTIONS MADE IN THE SIMPLIFIED ERM AND HEM



The simplified ERM is given by:

$$G = \left(\frac{dP_v}{dT}\right)_0 \sqrt{\frac{T_0}{C_{f\,0}}} \qquad (9.3)$$

It is recommended that the method given in equations (6.10) and (6.11) be used to obtain dP_v/dT (see also 6.5.2). The simplified ERM can be rewritten by making use of the Clausius-Clapeyron thermodynamic relationship which introduces the following further requirement:

g) That the mixture can be approximated as a single pseudo-component (see 6.3.3). (This will not be true for mixtures with a wide boiling range).

The alternative version of the ERM is given by :

$$G = \frac{h_{fg0}}{v_{fg0}\sqrt{C_{f\,0}\,T_0}} \qquad (9.4)$$

The simplified ERM is very convenient in that all the properties can be evaluated at the stagnation conditions in the reactor. The method may be appropriate for relief sizing for vapour pressure systems when flow is to be via a safety valve. Discharge coefficients for two-phase flow through safety valves are discussed in 9.7.1.

The version of the ERM given by equation (9.4) is used in Fauske's relief sizing method (see A5.3), together with a correction factor for friction if relief is via a bursting disc. Such correction factors are discussed further in 9.6.1.

A worked example of the use of the ERM is given in 6.5.

9.4.3 Tangren et al.'s method

Tangren et al.[6] proposed models for non-flashing two-phase flow. The simplest version of the model is given below, as used in references 10 and 11, and makes the following assumptions:

a) Frictionless flow.

b) No slip between the phases (slip will probably occur in practice but no slip is usually a conservative assumption).

c) Gas is an ideal gas.

d) Gas does not significantly dissolve in the liquid (possible overestimation of the relief capacity, which is non-conservative, has been reported when dissolved gas comes out of solution at the choke point[12]).

e) Thermal equilibrium between the phases.

f) The two-phase mixture is isothermal.

Assumption (f) of isothermal flow means that the method is different to the homogeneous equilibrium model (which assumes adiabatic flow). The difference between the two assumptions is usually small. The isothermal flow assumption gives a slightly simpler method and yields a conservative low value of G for relief sizing purposes. The DIERS Project Manual[11] gives the alternative version of Tangren et al.'s method, which assumes adiabatic flow and is therefore equivalent to the HEM.

The method requires the critical pressure ratio to be calculated first:

$$\eta_c = \left[2.016 + \left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714} \tag{9.5}$$

where α_0 is the void fraction entering the relief system from the upstream vessel. Flow will be choked if:

$$P_0\eta_c > P_a \tag{9.6}$$

where P_0 is the absolute pressure in the upstream vessel and P_a is atmospheric pressure in absolute units. In this case, η_c may be used for η in equation (9.8). Otherwise, for non-choked flow:

$$\eta = \frac{P_a}{P_0} \tag{9.7}$$

The value of G can now be calculated:

$$G = \sqrt{\frac{P_0}{v_0}}\,\frac{\left(\frac{2}{\alpha_0}\left[\left(\frac{1-\alpha_0}{\alpha_0}\right)(1-\eta)-\ln\eta\right]\right)^{0.5}}{\frac{1}{\eta}+\left(\frac{1-\alpha_0}{\alpha_0}\right)} \tag{9.8}$$

Although this method assumes frictionless flow, friction in short and uniform diameter vent lines can be accounted for by applying a discharge coefficient (see 9.6.1) or by use of a correction factor for vent-line friction. A conservative, low value of correction factor for gassy two-phase flow is obtained by assuming non-flashing, single-phase liquid flow and is given by equation (9.10).

A worked example of the use of Tangren et al.'s method is given in 7.6.

9.5 SELECTION OF CALCULATION METHOD FOR G FOR RELIEF SYSTEM SIZING

The selection of an appropriate calculation method is discussed in this section according to the system type for relief sizing (see 4.2).

9.5.1 Vapour pressure systems

Flashing two-phase flow calculations are appropriate for vapour pressure systems. Possible methods for calculating G for two-phase flashing flow are:

a) The Omega method, for turbulent flow, which is suitable for both flow calculations where friction is not significant, and for flow reduced by friction and static head change in long pipes of constant diameter. The method and full conditions of applicability are given in Annex 8. It can also be used for systems in which the diameter changes, although this procedure is time-consuming (see Annex 8).

b) The Equilibrium Rate Model (ERM) for turbulent choked flow. This neglects friction but a friction correction factor can be used in some cases. The method and full conditions of applicability are given in 9.4.2.

c) Suitable computer programs (see Annex 4). These are also likely to assume that flow is turbulent.

d) For viscous systems, methods suitable for laminar flow (see Chapter 10).

Section 4.4 discusses how to determine whether flow will be turbulent or laminar. It is important to do this because a larger relief system is likely to be required for laminar flow. For turbulent flow, the choice of method will depend on whether relief is via a safety valve or a bursting disc. Figure 9.4 may be used to select a method for calculating G.

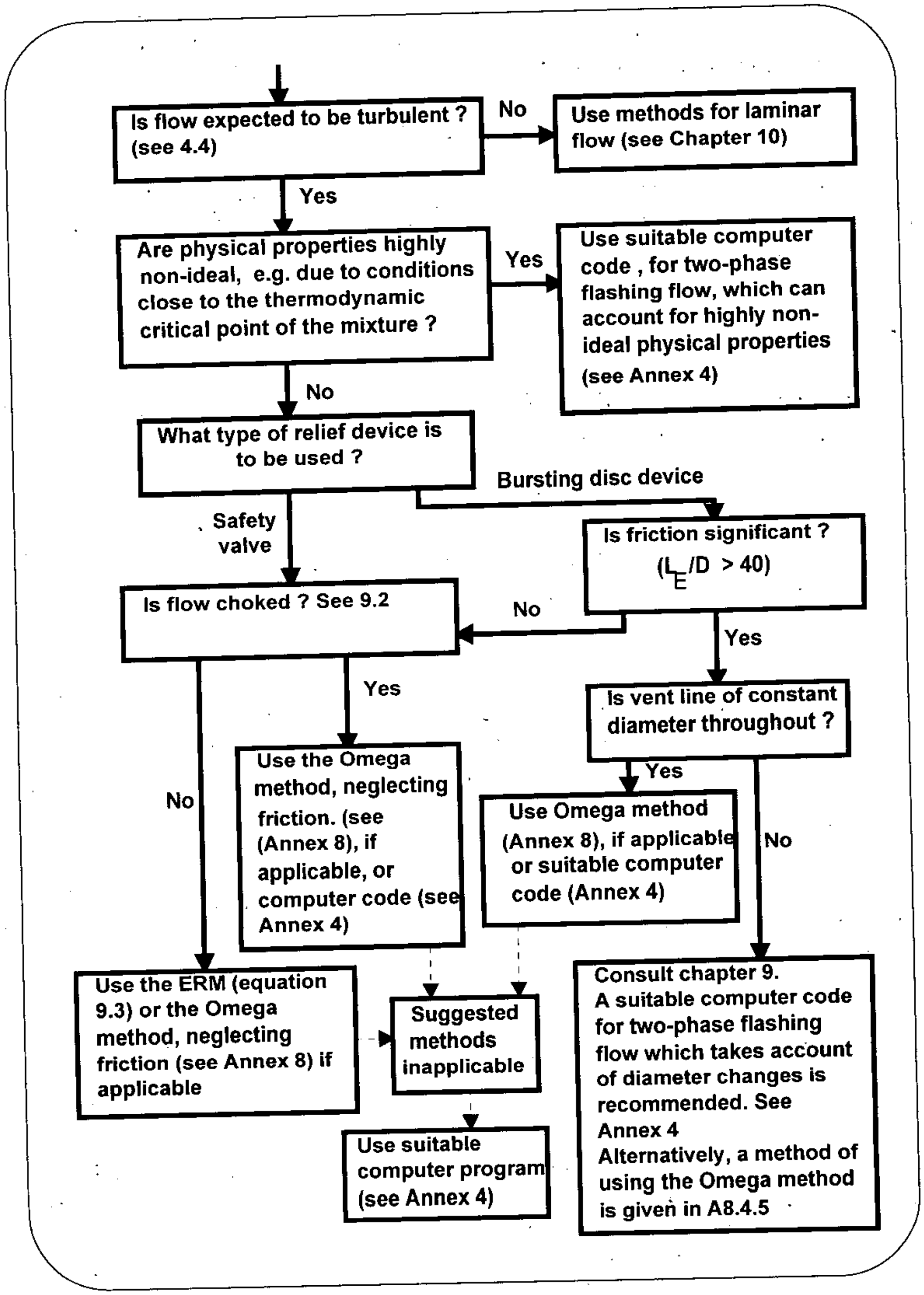
For other special cases (multiple liquid-phases and three-phase mixtures of vapour, liquid and suspended solids) advice is given in Chapter 10 on the applicability of the above methods.

9.5.2 Gassy systems

For gassy systems, G should be calculated assuming non-flashing two-phase flow, sometimes called "frozen flow". Possible methods for the calculation of G for gassy systems (using the homogeneous frozen flow model (HFM) which is a version of the HEM) are:

a) The Omega method for turbulent flow (see Annex 8). (Chapter 4 describes how to assess whether flow is turbulent). If relief is via a safety valve, then the version of the Omega method that neglects friction can be used. If flow is via a bursting disc, the Omega method allows account to be taken of friction in constant diameter vent lines. It can also be applied to vent lines with changing diameter by using a somewhat laborious procedure, described in A8.4.5.

Figure 9.4 DECISION TREE FOR SELECTING CALCULATION METHOD FOR G FOR VAPOUR PRESSURE SYSTEMS



b) Tangren et al's method. This method neglects friction but in some cases a friction correction factor may be used together with the method. See 9.4.3.

c) Suitable computer programs (see Annex 4). These are also likely to assume that flow is turbulent (see above).

d) Methods suitable for laminar flow (see Chapter 10).

For other special cases (multiple liquid-phases and three-phase mixtures of vapour, liquid and suspended solids), advice is given in Chapter 10 on the applicability of the above methods.

9.5.3 Hybrid systems

For hybrid systems, a method is needed for flashing two-phase flow in the presence of a non-condensible gas. Possible methods are:

a) The Omega method for turbulent flow (see Annex 8). (Chapter 4 describes how to assess whether flow is turbulent). If relief is via a safety valve, then the version of the Omega method that neglects friction can be used. If flow is via a bursting disc, the Omega method allows account to be taken of friction in constant diameter vent lines.

b) Suitable computer programs (see Annex 4). For hybrid systems, the computer code must be capable of handling multi-component mixtures with both volatile components and permanent gas components. Most such computer programs are likely to assume that flow is turbulent (see above).

c) Methods suitable for laminar flow (see Chapter 10).

For other special cases (multiple liquid-phases and three-phase mixtures of vapour, liquid and suspended solids) advice is given in Chapter 10 on the applicability of the above methods.

9.6 RELIEF PIPING FOR BURSTING DISCS

9.6.1 Bursting discs with short relief lines

When the line containing the bursting disc is short and the disc itself has low frictional resistance after burst (total equivalent length to diameter ratio less than about 40), the friction associated with the inlet contraction from the vessel will dominate the overall frictional effect on flow capacity. Also, the critical pressure ratio can be reasonably approximated to that for a nozzle (see Annex 8, Figure A8.2). This is needed to check that flow is choked.

The capacity of the relief system can be obtained from a two-phase flow calculation for nozzle flow. If the flow is not choked, then the Omega method (see Annex 8) or suitable computer code must be used to calculate flow capacity. For choked flow a larger range of methods may be applicable, e.g. ERM for vapour pressure systems (see 9.4.2) or Tangren et al.'s method for gassy systems (see 9.4.3), together with the application of a discharge coefficient. The capacity can then be obtained from:

$$G = C_D G_{nozzle} \tag{9.9}$$

Suitable values of discharge coefficient for different situations are given in BS 2915[13] for single phase liquid or gas flow. CCPS[14] indicate that a gas discharge coefficient should be used for two-phase flow provided the flow chokes, otherwise a liquid discharge coefficient should be used.

In the absence of a discharge coefficient, the most accurate way of estimating a flow reduction factor is to use the Omega method (see Annex 8). Alternatively, a discharge coefficient can be estimated from the following equation which applies for single-phase non-choked flow:

$$C_D = \frac{1}{\sqrt{1+K}} \tag{9.10}$$

where K is the number of velocity heads lost due to friction in pipes and fittings. It is important to include the frictional resistance of the inlet contraction from the vessel to the vent pipe. The number of velocity heads lost in a typical non-rounded inlet contraction is 0.5[15]. Thus:

$$K = 0.5 + \frac{4fL}{D} + \Sigma K_{fittings} \tag{9.11}$$

Typical values of number of velocity heads lost, $K_{fittings}$, and equivalent lengths, L, of fittings which may sometimes be found in relief lines are given by CCPS[14].

A value for 4f of 0.02 is often used for turbulent two-phase flow. A plot of the friction factor, f, as a function of Reynolds number and relative roughness (the ratio of roughness length to pipe internal diameter) is given in most texts on fluid flow, e.g. reference 15. However, calculating the Reynolds number for two-phase flow is not straightforward because it is unclear what viscosity to use. Provided the liquid is relatively low viscosity (< 100cP) and the upstream pressure is high enough to be sure that the flow will choke, it will often be reasonable to assume the flow is in the highly turbulent region of the friction factor plot for which the friction factor is independent of Reynolds number.

Once K is known, it is possible to estimate a correction factor to the frictionless flow rate (calculated using the ERM or Tangren et al.'s method) which takes account of friction. The most accurate way of doing this is by using a method which takes account of the compressibility of the two-phase fluid. The Omega method (see Annex 8), when applicable, is one way of doing this. A graph of effective discharge coefficient versus number of velocity heads lost for different values of Omega is given by DIERS[16].

Alternatively, equation (9.10) gives an approximate value for the correction factor. For the ERM, Fauske[17] gave a Table of friction correction factors as a function of the equivalent length to diameter ratio. These are given in Table 5.1 and tend to be quite conservative compared with values estimated using the Omega method.

Table 5.1 Friction correction factors for use with the simplified ERM[17]

L_E/D	F
0	1
50	0.87
100	0.78
200	0.68
400	0.57
600	0.5

9.6.2 Bursting discs with long relief lines of uniform diameter

It is usual for a disc to be specified to be the same diameter as the piping. When a bursting disc opens as intended, the flow area is close to the pipe cross-sectional area, and choking at the disc itself is not therefore expected. (An exception may be if a permanent vacuum support reduces the flow area through the disc assembly, in which case the method given in 9.6.3 below should be used). The flow capacity of a bursting disc system is determined by the piping system, rather than by the disc itself.

In order to size the relief piping, the total equivalent length of piping should be evaluated. This is the sum of the actual length and the equivalent length of pipe fittings such as bends and the disc itself. DIERS[18] suggest that the equivalent length of most discs is given by $L/D \doteq 16$, but that $L/D = 50$ or more may be required for some discs. (L/D greater than 1000 is possible for some discs installed with vacuum support and insulation. However, in cases of such very high L/D it is important to check for a reduction in flow area across the disc which may cause choking). The frictional resistance of a burst disc, in terms of L/D or number of velocity heads lost, K, is sometimes available from bursting disc manufacturers for particular disc designs. If there is significant static head change between the start and end of the relief line (10% of the gauge disc bursting pressure or more), then the magnitude of the overall static head change should also be evaluated.

The flow capacity of any particular diameter line can then be evaluated using the HEM. Simplified methods such as the ERM (see 9.4.2) or Tangren et al's method (see 9.4.3) are not appropriate for long or complex relief lines because they assume choked flow and do not include any method for checking that this is the case. In many cases, for turbulent flow, the Omega method implementation of the HEM (see Annex 8) can be used. If the relief line is of constant diameter, then the Omega method may be applied directly. The method will involve the following steps:

a) Evaluate the two-phase choked G for a nozzle (i.e. for frictionless flow).

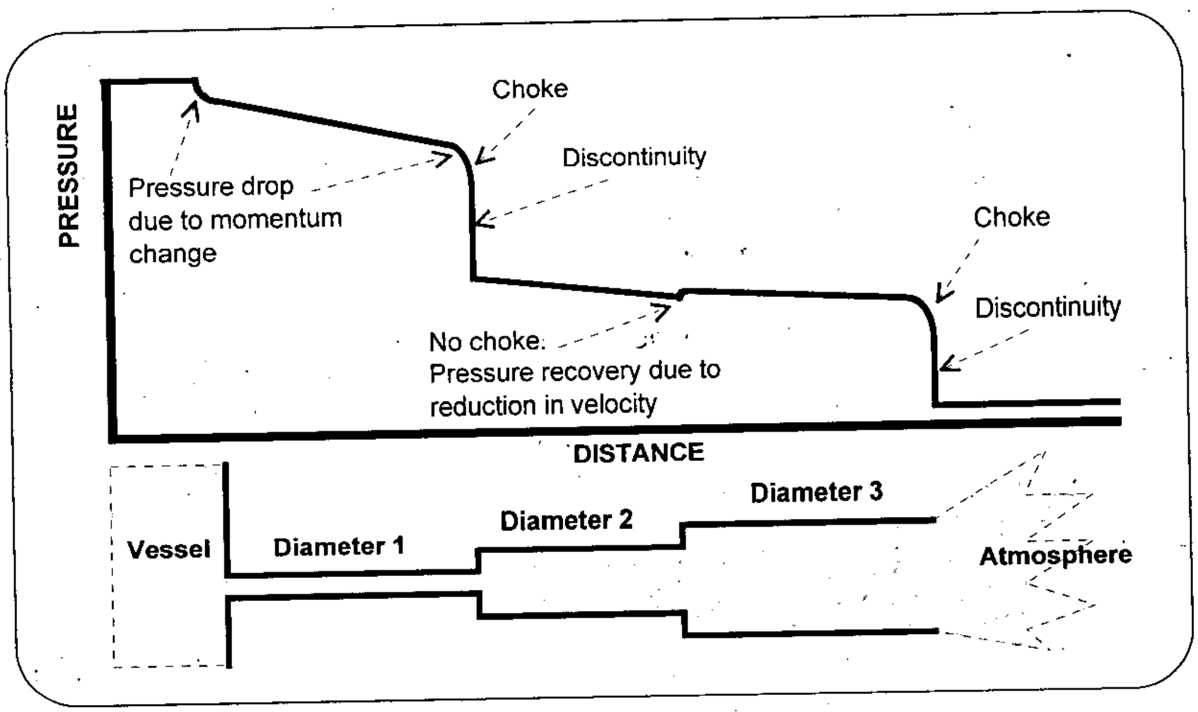
b) Apply a correction factor for vent line friction and any significant upwards static head (height) change.

c) Determine whether or not flow will indeed be choked, and, if not, apply a correction factor for the actual back pressure.

9.6.3 Bursting discs with long relief lines of changing diameter

If the relief line contains changes in diameter, then each expansion is a potential choke point (see 9.2 and Figure 9.5). Simpson[2] suggests a calculation procedure which can be used in such cases. A number of computer codes can be used for relief lines of changing diameter (see Annex 4).

Figure 9.5 EXAMPLE OF PRESSURE DISTRIBUTION ALONG RELIEF LINE WITH MULTIPLE CHOKE POINTS



The Omega method is intended for constant diameter relief lines. However, it is possible to use the Omega method in an iterative calculation procedure if the use of a hand calculation method is preferred. A suggested procedure for using the

Omega method to find the capacity of a bursting disc line with two sections having different pipe diameters is given in A8.4.5.

9.7 RELIEF PIPING FOR SAFETY VALVES

9.7.1 Safety valve capacity for two-phase relief

Safety valve manufacturers provide discharge coefficients for the flow of single-phase gas or liquid through their valves at a particular overpressure, chosen to ensure that the valve is fully open (see 5.2.2). These discharge coefficients have usually been obtained by flow testing and de-rating of the measured discharge coefficient to 90% of the measured value[19]. Graphs are available for further reducing the discharge coefficient for high viscosity flow[20,21]. CCPS[14] indicate that a gas/ vapour discharge coefficient should be used for two-phase flow provided the flow chokes, otherwise a liquid discharge coefficient should be used.

Research is currently being carried out for DIERS and in Europe to measure safety valve discharge coefficients for two-phase flow, including high viscosity systems. Note that any two-phase discharge coefficient is the ratio of measured flow to flow calculated using a particular two-phase flow model. Discharge coefficients should therefore only be used with the flow model for which they were derived.

Note that it is also worthwhile to find the actual nozzle flow area for a particular valve, since there is some variation in this between different manufacturers, even for standard nozzle sizes. The standard nozzle sizes (rather than the actual sizes) for safety valves are defined in references 19 and 22.

For safety valves, the flow capacity can be estimated using any applicable implementation of the homogeneous equilibrium model for frictionless flow, together with an appropriate discharge coefficient (see above). This may be the Omega method (see Annex 8) or a suitable computer code. For flashing two-phase flow through safety valves (i.e. for vapour pressure systems), the simplified equilibrium rate model (see 9.4.2), if applicable, may perhaps be used instead of the homogeneous equilibrium model because it gives approximately the same result (typically a flow rate 10% higher than HEM). Consideration should be given to including a safety factor of at least 10% to the ERM to account for differences with the HEM. For gassy systems, Tangren's method (see 9.4.3) may be used instead of the homogeneous equilibrium method because it is conservative in that it yields slightly lower flow rates.

DIERS[23] commissioned research into the stability of safety valves in flashing liquid service. They found that choking could occur in the outlet of the valve body in some situations, giving rise to excessive back pressure (see 9.7.3) and valve instability (rapid cycling between open and closed). This becomes an increasing problem for larger valve sizes, in which the ratio of valve body outlet area to nozzle area becomes increasingly smaller for standard valve dimensions[22]. It should be checked whether or not a choke in the valve body will cause excessive back pressure by the procedure given in 9.7.3. If such a choke in the outlet of the valve could occur, it may be necessary to consult valve manufacturers in order to obtain a valve with a non-standard, larger outlet size.

Safety valve instability must be avoided. The rapid cycling of the valve from open to closed (chattering) can destroy the valve. Resonance could, in certain circumstances, lead to fracture of the associated piping. Furthermore, the capacity of a safety valve during cycling will be considerably less than if it remained fully open, and is very likely to be insufficient to prevent overpressurisation of the upstream vessel.

9.7.2 Piping upstream of safety valves

It is generally recommended that the frictional pressure drop in the piping between the vessel and the safety valve inlet should be limited to no more than 3% of the gauge set pressure of the safety valve[19] in order to prevent instability. This instability occurs because when the valve is closed, there is no flow and no pressure drop, so that the pressure in the reactor is high enough to open the valve. However, when flow develops the upstream pressure drop causes the pressure at the valve to be too low to keep it open and results in chattering.

Only the irreversible frictional pressure drop should be included in the calculation of upstream pressure drop, not the momentum pressure drop required to accelerate the fluid to the velocity at inlet to the valve. The irreversible frictional pressure drop includes both friction in the inlet contraction from the reactor (K = 0.5 for a sudden contraction[15]) and friction in the piping, bends and any fittings.

In order to achieve a frictional pressure drop of less than 3%, the inlet piping should be as short and simple as possible. However, for many duties on chemical reactors, a bursting disc will be required upstream of the safety valve, to protect it from possible blockage. Such systems often use duplicate safety valves with interlocked valve arrangements. In such cases, it may be necessary to increase the inlet piping diameter above that of the valve inlet diameter, in order to conform with the 3% pressure drop requirement. The total equivalent length of inlet piping, including the friction in contractions, bends and any valves and bursting discs should be calculated.

The calculation of the inlet frictional pressure drop can be done using the HEM model for two-phase flow. A simplified conservative calculation may be made by assuming incompressible flow, with a two-phase density equivalent to that at the inlet to the safety valve:

$$\Delta P = \frac{1}{2}\rho u^2 \frac{4fL}{D} \qquad (9.12)$$

where ρ is the two-phase density at the inlet to the safety valve. An approximate value for this can be obtained by assuming the vessel is at the set pressure plus 3%

of the gauge set pressure and carrying out an isenthalpic flash calculation (see Annex 9) to the set pressure in order to determine the fraction of vapour.

The flow rate used for this calculation should be the best estimate flow rate for the safety valve. BS 6759[19] requires that any safety factors used in determining G for relief system sizing, including the 10% de-rating of the safety valve discharge coefficient, should be removed. The actual flow area through the valve should be used.

A value for 4f of 0.02 is often used for turbulent two-phase flow (see 9.6.1).

An alternative, more rigorous procedure than equation (9.12) above, using the Omega method, is given by Leung[4].

9.7.3 Back pressure on safety valve

The built-up back pressure on a safety valve (i.e. that resulting from the flow downstream of the valve) needs to be limited in order to prevent instability of the valve. The maximum allowable built-up back pressure depends on the valve design, but is often 10% of the gauge set pressure for conventional safety valves and can be up to about 30% for balanced valves. (High back pressures for balanced valves will tend to reduce the valve capacity and this needs to be taken into account in sizing the valve.) The valve manufacturer should be consulted about the maximum back pressure for a particular valve design and application[19]. The built-up back pressure should be evaluated at the best estimate flow capacity for the valve, using the actual flow area through the valve. Any safety factors used in determining G for relief system sizing, including the 10% de-rating of the safety valve discharge coefficient, should be removed.

The back pressure on the safety valve due to the flow through the discharge line can be calculated using a suitable computer program (see Annex 4). However, the Omega method (see Annex 8) can also be used to check that the back pressure is not excessive, if it is applicable and if the discharge piping from a safety valve is of constant diameter.

Knowing the maximum allowable back pressure on the safety valve, an isenthalpic flash calculation can be performed from the upstream vessel conditions, to find the conditions at the maximum allowable back pressure. The Omega method can then be used to find the flow rate through the discharge piping, with the upstream pressure for calculation of Omega at the maximum allowable back pressure and the downstream pressure at atmospheric. If this calculated flow rate exceeds the best estimate safety valve capacity, then the actual back pressure will be less than the maximum and the proposed design is acceptable. The actual back pressure could then be obtained by a trial-and-error procedure, varying the assumed back pressure until the calculated flow rate equals the best estimate safety valve capacity. The total equivalent length of the piping, including bends and any other fittings, should then be evaluated. The back pressure to which the piping discharges also needs to be known. This will either be atmospheric, or the operating pressure of any disposal system.

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CHAPTER 10

SPECIAL CASES

10.1 INTRODUCTION

The purpose of this chapter is to give sources of additional information for several cases which modify the relief sizing from the methods given in Chapters 6-8. Those cases which are covered in this chapter are:

a) Viscous systems: If the viscosity is high enough, then the flow in the relief system may be laminar rather than turbulent. 4.4 and Annex 2 give methods for determining whether laminar flow is expected. 10.2 below discusses the sizing of relief systems in cases where laminar flow is expected.

b) The effect of solids: Many industrial reactions involves solids, so that flow in a relief system is of three phases (gas or vapour/ liquid/ solid). 10.3 below discusses corrections that can sometimes be made to the liquid physical properties to account for the presence of solids.

c) The effect of two liquid phases: Some industrial reactions involve two immiscible liquids. This gives rise to a three phase system (gas or vapour/ liquid/ liquid). Relief sizing in such cases is discussed in 10.4 below.

10.2 HIGH VISCOSITY SYSTEMS

10.2.1 General comments about flow of viscous fluids

The viscous systems that are of most concern are those which may give rise to laminar flow in the relief system. The level swell in the vessel may also be affected. These two topics are covered below. It should be noted that only moderately high viscosities, of 100 cP or more, may be sufficient to cause laminar flow or to change the level swell behaviour. Failure to take account of the effects of laminar flow could lead to the serious undersizing of the relief system.

In addition, some very viscous fluids may give experimental difficulties in calorimetric measurement of the rate of reaction. The magnetic stirrer in the original design of the DIERS bench-scale apparatus is unlikely to cope with high viscosity. Some other types of calorimeter use mechanical agitation which may be better. If a highly viscous fluid is a reactant, loading of the test cell may be difficult. This will also be the case if a highly viscous product is to be used in a depressurisation test for scale-up of the relief flow rate. Some alternative designs of test cell are available with a larger opening. (See Annex 2 for descriptions of suitable calorimeters.)

High viscosity materials are more likely than low viscosity fluids to cause problems due to deposition and possible blockage. Some types of viscous fluids may solidify in the relief piping. This may be true of dilatant fluids (see 10.2.2 below), whose viscosity increases with shear rate, if this behaviour has not been properly taken into account in the relief system design. Pseudoplastic fluids (see 10.2.2), whose viscosity decreases with shear rate, may cause blockage towards the end of relief when the reactor pressure is no longer high enough to give a high flow rate (and consequent high shear rate).

If a safety valve is to be used for relief, it may be advisable to install a bursting disc upstream of the valve to reduce the likelihood of the valve seat sticking shut. In such cases, the space between the valve and disc should be monitored for any pressure build up due to leakage in either direction. The space between the disc and safety valve could also be vented to a safe location (although a small diameter vent line might block if the fluid is viscous). Such a vent may be fitted with an excess flow valve to prevent loss of contents in the event of pressure relief[1]. Discs which could fragment and cause blockage of the safety valve, e.g. graphite discs, should not be used in this application. It may also help to install the relief system off a low viscosity liquid inlet line (of suitable diameter) to minimise the possibility of deposition on the underside of the disc.

Viscous relief is best avoided, if at all possible. If the high viscosity occurs towards the end of a reaction (e.g. polymerisation), a low relief pressure may help, by ensuring a relatively low conversion at the point when the relief system operates[2].

Viscous systems are the subject of continuing research by the US DIERS Users Group and in Europe. Research projects include the flow of high viscosity two-phase mixtures in safety valves, and the effect of bends and pipe fittings on high viscosity two-phase flow in pipes.

10.2.2 Laminar flow in the pressure relief system

<u>General</u>

The effect of laminar flow in the relief system can be to reduce the flow rate compared with that for turbulent flow by an order of magnitude. 4.4 and Annex 2 describe how to determine whether or not flow will be laminar. In the case of laminar flow, this section gives methods for calculating the mass vent capacity per unit area, G. This value of G can then be used together with relief sizing methods given in chapters 6-8 to find the relief size required.

Laminar flow is known to reduce the capacity of safety valves for single-phase liquid flow and a capacity correction chart is available[3,4]. The derivation of this chart has recently been reviewed[5] and this review gives additional information about the applicability of the correction factor to different sizes of valve.

DIERS experimental work[2] found that, for high viscosity flashing flows, expanding the diameter of the piping downstream of a flow restrictor (which was close to the upstream vessel) increased the flow rate to close to that for turbulent flow. This was probably due to a flow regime change after the restrictor to vapour-continuous rather than liquid-continuous. Thus, increasing the diameter downstream of the relief device may be beneficial for high viscosity systems, but DIERS did not have enough experimental data to propose a design method based on this phenomenon.

High viscosity fluids may behave in a number of different ways:

a) Newtonian fluids in which the shear rate (velocity gradient with radial distance in a pipe) is proportional to the shear stress (due to the pressure gradient along the pipe). In this "ideal" case, the viscosity is the proportionality constant.

b) Pseudoplastic (shear-thinning) fluids in which the viscosity decreases as the shear rate increases.

c) Dilatant (shear-thickening) fluids in which the viscosity increases as the shear rate increases.

d) Viscoelastic fluids in which the fluid possesses both viscous and elastic properties.

The characterisation of the viscosity is difficult for non-Newtonian fluids because the viscosity changes as a result of the flow process, which increases the shear rate. This is further complicated for two-phase fluids because the presence of bubbles will also affect the viscosity. The simpler methods to obtain G for high viscosity fluids make the simplifying assumptions that the fluid viscosity is equal to the liquid viscosity and that the fluid is Newtonian.

A number of methods have been proposed for the calculation or scale-up of G for laminar flow of flashing liquids. Figure 10.1 is a decision tree to aid selection.

<u>Applicability of simple methods for obtaining G for laminar two-phase flow</u>

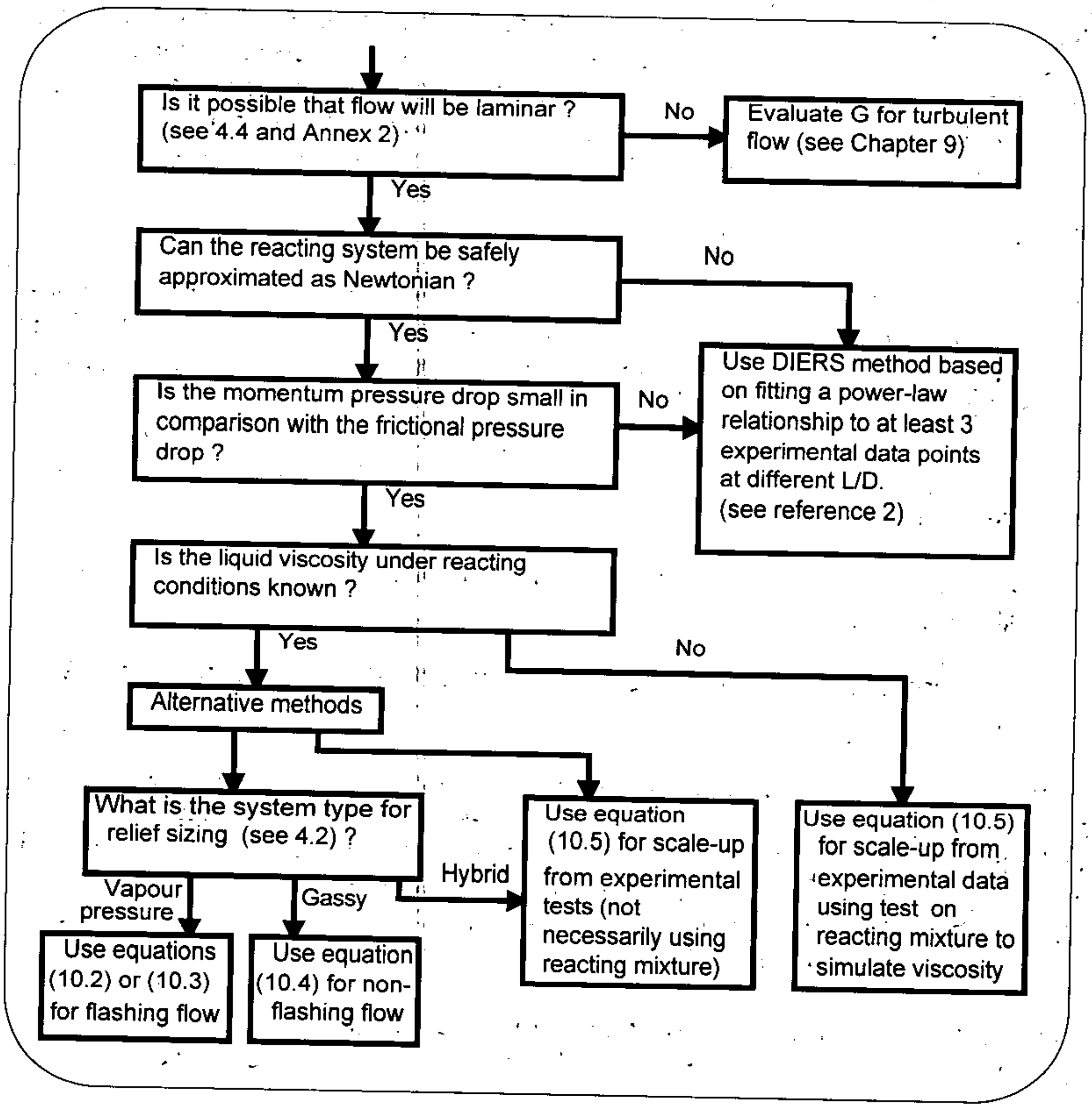
This methods given below in equations (10.2) to (10.5) make the following assumptions :

a) Flow is expected to be laminar. DIERS[2] give an applicability criterion for the methods below:

$$\frac{G_L}{G_{T\,(calculated)}} < 0.2 \qquad (10.1)$$

G_L is determined by test (see Annex 2). The calculation of G_T using the Omega method for turbulent flow is described in Annex 8.

Figure 10.1 **DECISION TREE TO SELECT METHOD FOR EVALUATING G FOR LAMINAR FLOW**



b) The two-phase viscosity can be approximated by the liquid phase viscosity.

c) The fluid is Newtonian (or this can be assumed as a safe approximation). If the fluid is actually pseudoplastic, it is likely to be safe to use a viscosity measured at zero shear rate (no flow) in the equations below. Use of this method for a dilatant fluid is unlikely to be safe, unless a viscosity is available at the maximum shear rate which will be experienced in the full-scale vessel.

d) The momentum pressure drop is small in comparison with the frictional pressure drop. This is likely to be the case for laminar flow unless the relief system is extremely short. In such cases, the minimum of G calculated by this method and that for turbulent frictionless choked flow (see Chapter 9 and Annex 8) should be used.

e) The relief line is horizontal (or the static head change is small enough to ignore) and of constant diameter.

Calculation of G for Newtonian laminar flashing two-phase flow

This method[2] is applicable if the above assumptions are valid and the flow is of a flashing liquid. The method makes use of the simplified Equilibrium Rate Model (ERM) (see 9.4.2).

G is given by:

$$G_L = \left(\frac{dP_v}{dT}\right)^2 \left(\frac{T}{C_f}\right) \left(\frac{1}{32\mu_f}\right) \left(\frac{D}{L/D}\right) \tag{10.2}$$

An alternative version, utilising the alternative version of the ERM (see 9.4.2) is:

$$G_L = \left(\frac{h_{fg}}{v_{fg}}\right)^2 \left(\frac{1}{T C_f}\right) \left(\frac{1}{32\mu_f}\right) \left(\frac{D}{L/D}\right) \tag{10.3}$$

Calculation of G for Newtonian laminar non-flashing two-phase flow

This method[2] can be used if the assumptions given above are valid and if the flow is of a non-flashing two-phase mixture:

$$G_L = (1-\alpha_0)\rho_{f0}(P_0 - P_a) \left(\frac{1}{32\mu_f}\right) \left(\frac{D}{L/D}\right) \tag{10.4}$$

Evaluation of G by scale-up of experimental test data for Newtonian fluids

This method[2] can be used if the assumptions given above are valid. A small-scale test needs to be performed in which laminar flow is obtained (see Annex 2) at the same L/D ratio as will be the case for the full-scale plant. The basic scale-up equation (based on equation (10.2)) is:

$$G_L = G_{Le} \left(\frac{D}{D_e}\right) \left(\frac{(dP_v/dT)}{(dP_v/dT)_e}\right)^2 \left(\frac{T}{T_e}\right) \left(\frac{C_{fe}}{C_f}\right) \left(\frac{\mu_{fe}}{\mu_f}\right) \tag{10.5}$$

Analogous equations can also be written based on equations (10.3) and (10.4) as required.

This equation can be used in a number of different ways, depending on how the experimental test has been conducted. Ideally, the test should be conducted in such a way as to make all the ratios equal to unity except for the diameter ratio. If this is done, then the test will effectively remove any uncertainties associated with the two-phase viscosity. However, this may not be conservative in cases where the mixture is not really Newtonian, since the viscosity will depend on the shear rate in the test which will not scale-up. In such cases, if data are available on the liquid viscosity, careful use can perhaps be made of the viscosity ratio in the equation in order to obtain a conservative value of G.

Experimental testing with highly viscous fluids can be difficult. It may be easier to test a non-reacting mixture of the same material (for example, polymerisation reaction products) as a worst case, rather than attempt to use a small-scale test. This may have relatively poor agitation, and would poorly simulate the plant-scale reaction. If so, equation (10.5) can still be used for scale-up, but values of dP_v/dT will have to be obtained separately.

Other methods

The DIERS Power Law Scaling Method[2] is more robust than those given above and is applicable to fluids which are not Newtonian. The fluid is assumed to obey a power law and the power law parameters are assumed constant along the length of the relief line. Several experiments, at different L/D are required to fit the power law correlation, which may then be used to obtain G. Full details are given in reference 2.

Morris et al.[6] have proposed a graphical method for estimating vent flow rate for high viscosity flashing fluids. The method is semi-empirical and is fitted to experimental data for fluids with viscosities up to 750 cP.

10.2.3 Effect of viscosity on level swell

The effect of moderately high viscosity (> 100 cP) is to prevent the formation of the churn-turbulent flow regime so that the bubbly flow regime persists at higher superficial gas/ vapour velocities (see Annex 3).

Considerable work has been done at JRC Ispra to visualise level swell for viscous fluids[7,8,9]. This indicates that at moderate viscosity (around 100 cP) foaming behaviour of the fluid (if it occurs) dominates viscous effects. Many high viscosity fluids are foamy because they are not pure fluids. At higher viscosities, approaching 1000 cP, there appears to be much less foaming and the flow characteristics are dominated by viscous effects.

Experimental work for highly viscous fluids suggests that some disengagement does occur, in that bottom-vented test results are different from top-vented test results[2]. The flow regime in highly viscous flow (>1000 cP) is unlikely to be one of those (churn-turbulent or bubbly flow) described in Annex 3.

Since bubbly flow at high superficial velocity approximates to homogeneous flow, this could lead to the conclusion that the homogeneous vessel assumption is likely to be good for high viscosity systems.

10.3 THE EFFECT OF SOLIDS

10.3.1 Effect of solids on calorimetry

If solids are present in the reactor, as reactant, catalyst, product or even as inert material, then experimental difficulties may be posed:

a) Unless the particle size is very small, there may be difficulties in loading solids into the standard type of test cell for the DIERS bench-scale apparatus or the RSST (see A2.2.2). This can sometimes be overcome by using modified test cells with larger openings. The problem is less for adiabatic Dewar calorimetry because of the larger dimensions of the Dewar (see A2.2.3).

b) There may be difficulties in the calorimetric measurement of reaction rate because the solid particles may increase the mixture viscosity to the point where the agitation becomes inadequate. This will particularly be the case for magnetic stirrers.

c) If the solid is a reactant or catalyst, the reaction may be diffusion-controlled in some cases, rather than controlled by the chemical kinetics. It may be difficult to obtain reliable adiabatic rate data in such cases because the reaction rate will be significantly affected by the agitation efficiency and it may be difficult to simulate this in a small-scale calorimeter. It is advisable to investigate the sensitivity of experimental results to agitation so that this can be taken into account.

10.3.2 Effect of solids on relief sizing equations

Thought should be given as to whether the solid reactants will be entrained out of the reactor in the relief stream. In most cases, this is likely to be true as good dispersion of the solid particles in the liquid phase will be required for process reasons. However, if it is decided that the solid particles would remain in the reactor, a number of relief sizing methods may be invalid. For example, Leung's method for vapour pressure systems (see 6.3) assumes that the heat generation rate in the reactor is proportional to the total mass remaining in the reactor. If solid reactants (or possibly catalysts) were being concentrated in the reactor, this assumption could be invalid. In such cases, it may be necessary to use a suitable computer simulation for relief sizing (see Annex 4).

If it is decided that the relief sizing equations are valid, then the liquid physical properties should be modified as listed below to take account of the presence of the solid. This should yield a safe relief size:

a) The mass of liquid plus solid should be used in place of the mass of liquid.

b) q, the heat release rate per unit mass of reactants, should be expressed in terms of the mass of liquid plus solid.

c) An average density for the liquid and solid should be used.

d) Consideration should be given to whether the solid particles are small enough to be in thermal equilibrium with the liquid. If this will be the case, then an average heat capacity should be used. If the solid temperature is expected to lag behind that of the liquid, then a safe assumption is that the solid has zero heat capacity, i.e:

$$\overline{C_f} = C_f\left(\frac{m_f}{m_f + m_s}\right) \qquad (10.6)$$

e) Latent heat and vapour density should be evaluated on the basis of the composition of the vapour composition, and so will not be affected by the presence of solids.

f) The relief system capacity per unit area should be evaluated as discussed in 10.3.3 below.

10.3.3 Effect of solids on relief system flow capacity

Two possible effects of solids on the relief system capacity are:

a) total blockage and/ or failure of the relief system to operate;

b) possible reduction in the relief system capacity.

<u>Blockage or failure to operate</u>

If solids are allowed to accumulate on the underside of a bursting disc or safety valve, then it is likely that the relief device will not operate when required, at least not at the required set pressure. Safety valves may be more vulnerable in this respect than bursting discs, and it is common practice to fit a bursting disc upstream of the safety valve to protect it. Further information is given in 10.2.1 and reference 1.

Provision should also be made to minimise solids build-up under a bursting disc. If the solid may be present due to freezing, then heat tracing may be a solution. In other cases, it may be beneficial to take the relief system off a liquid inlet nozzle (of suitable size) so that the nozzle is washed clean of solids by the liquid.

Cases in which a relief system opened and subsequently blocked due to the flow of solids are rare. However, if large lumps of solid can be formed, with a diameter of the same order as the relief line size, then blockage could occur. This can be the case for polymerisations under some conditions. The flow path through a safety valve is much smaller than that through a disc, so the use of safety valves in such cases should be avoided. Another cause of blockage is freezing of the relieving fluid in a cold relief line. This is a particular problem if relief at low rate occurs either at the start or end of a runaway. Heat tracing or jacketing of the relief line is a possible solution, but care should be taken to ensure the integrity of such a system.

If it is not possible to be confident that the relief system will operate without blockage, then consideration should be given to installing further measures to prevent runaway occurring and/ or the use of alternative measures to mitigate its effects (see Annex 1). Unfortunately, the same mechanisms by which a relief system may be expected to block may also cause blockage of pressure or temperature measurement points within an instrumented protective system, so care should be taken in such cases.

Reduction of relief system capacity

The presence of solids will act to reduce the relief system capacity below that for liquid alone because of the following:

a) The solids must also be accelerated to the relief system outlet velocity and the effect of density on static head also needs to be taken into account. An average density for the liquid and solid should be used in the calculation of G, e.g. when using the Omega method (see Annex 8).

b) The presence of solids will tend to increase the liquid viscosity. The mixture viscosity, including the effects of solids, should be used whenever it is required in calculations. If the mixture viscosity exceeds about 100 cP, then section 10.2 of this chapter should also be consulted. The viscosity is only important for the calculation of G if laminar flow results. Particular care must be taken for flashing systems containing dissolved solids as the viscosity can be greatly increased during relief as flashing of the liquid concentrates the solid.

c) For flashing fluids, the heat capacity of the solids will increase the amount of flashing and may lead to choking at a lower flow. The safe assumption is to use the average specific heat capacity of the liquid and solid, even if complete thermal equilibrium is not expected, i.e.

$$\overline{C_f} = \frac{m_f C_f + m_s C_s}{m_f + m_s} \qquad (10.7)$$

10.3.4 Effect of solids on level swell

The main effect of the presence of solids on level swell will be in changing the liquid viscosity. The mixture viscosity should be used in place of the liquid viscosity in level swell correlations.

10.4 EFFECT OF TWO LIQUID PHASES

10.4.1 Effect of two liquid phases on calorimetry

Many commercial reactions employ two liquid phases in which the reaction takes place at the interface between the phases. For this type of reaction, the interfacial area may have a strong effect on the reaction rate and this will be affected by the agitation. Similar or greater agitation than that at plant scale should be provided within the calorimeter. This may be best achieved by a calorimeter incorporating a mechanical agitator. It may be difficult to obtain reliable adiabatic rate data in such cases because the reaction rate will be significantly affected by the agitation efficiency and it may be difficult to simulate this in a small-scale calorimeter. It is advisable to at least investigate the sensitivity of experimental results to agitation. It may be possible to arrive at a suitable safety factor in this way.

10.4.2 Effect of two liquid phases on worst case

In some cases the worst case for relief sizing may be agitator failure, particularly if a more reactive, more volatile layer could form on top and then run away without the diluting effect of the more dense layer.

10.4.3 Effect of two liquid phases on relief sizing equations

If the reactor contains two immiscible liquid phases, the calculation of vapour pressure in the reactor needs to take account of this. For a completely immiscible system, the total vapour pressure will be given by the sum of the vapour pressures of each phase.

Departure from vapour/ liquid equilibrium within the reactor may be more marked for a two-liquid-phase system than for one with a single liquid phase. Bubble nucleation within the dispersed phase may be difficult and this can lead to considerable superheating of this phase. Relief sizing methods generally assume that vapour/ liquid equilibrium is maintained in the reactor during relief. However, superheating could be so great for two-liquid-phase systems (in which the volatile phase is dispersed) that this assumption is invalid and expert guidance should be sought.

The effect of vapour/ liquid non-equilibrium in the vessel is to reduce tempering, so that the temperature and reaction rate increase, but the pressure is lower than the equilibrium pressure at that temperature which balances the effect.

10.4.4 Effect of two liquid phases on relief flow capacity

There are three main effects[10]:

a) The vapour pressure needs to be calculated in a way that takes account of the presence of two liquid phases. Methods such as the Omega method (see Annex 8) will be inapplicable unless this is done. A computer code may alternatively be used to evaluate G (see Annex 4), but care needs to be taken to ensure that it is suitable for two-liquid-phase systems. Alternatively, if the volatile phase is the continuous phase (see also (c) below), and friction is not significant, the Equilibrium Rate Model can be used to find G (see 9.4.2). The version of the ERM given by equation (9.3) is recommended, in which dP/dT is evaluated for the two-liquid-phase system and the average liquid specific heat capacity is used.

b) The heat capacity of the less volatile phase will increase the degree of flashing of the more volatile phase. This can lead to choking at a lower flow rate, and so needs to be modelled by a suitable computer code when friction is significant (see (a) above).

c) If the more volatile phase is the continuous phase, there is no change to non-equilibrium flow effects (see Chapter 9) compared with a single liquid phase. However, if the volatile phase is dispersed, non-equilibrium flow can occur for much longer pipe lengths than the 0.1 m length criterion for a single phase liquid. For relief sizing, it is conservative to ignore this and assume equilibrium flow. However, it could greatly increase the required size of any disposal system (see Chapter 11) and the pressure drop upstream and downstream of safety valves (see Chapter 9). In such cases, the homogeneous frozen flow model (see 9.3.2) could be used. One way of implementing this is to model the system as a gassy system using the Omega method (see Annex 8).

10.4.5 Effect of two liquid phases on level swell

The presence of two liquid phases is likely to cause a fluid to be inherently foamy and so give rise to homogeneous vessel behaviour.

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CHAPTER 11

DISPOSAL SYSTEMS

11.1 INTRODUCTION

A full treatment of the selection and design of disposal systems for the safe handling of the effluent from reactor relief systems is beyond the scope of this Workbook. A book on the subject[1] has recently been published by CCPS (the Center for Chemical Process Safety of the American Institute of Chemical Engineers). Useful information is provided by Huckins[2] (including extracts from the CCPS book), DIERS[3] , Parry[4] and Singh[5].

In many cases it will not be acceptable to relieve a two-phase reacting mixture direct to the atmosphere. Factors to be considered[2] include:

a) toxicity;

b) corrosion;

c) flammability;

d) health risk;

e) public nuisance.

The design of a treatment or disposal system for the effluent from a reactor relief system needs to consider whether the reacting mixture will continue to react, unless the disposal system is designed to stop further reaction. It is not acceptable to simply move the hazardous condition from the reactor to a disposal vessel.

Appropriate mechanical design of disposal systems is important. In some cases, the disposal system may need to be a pressure vessel. Mechanical design requirements for disposal systems are addressed in references 3 and 4.

It should be noted that "rules of thumb" giving a ratio of the volume of the containment/ disposal system to the volume of the reactor may result in vast undersizing and could lead to overpressurisation of the reactor and relief system during a runaway incident.

Although environmental protection must not compromise safety, there is a duty to minimise harm to the environment from prescribed processes at all times. There is a hierarchy of needs which includes:

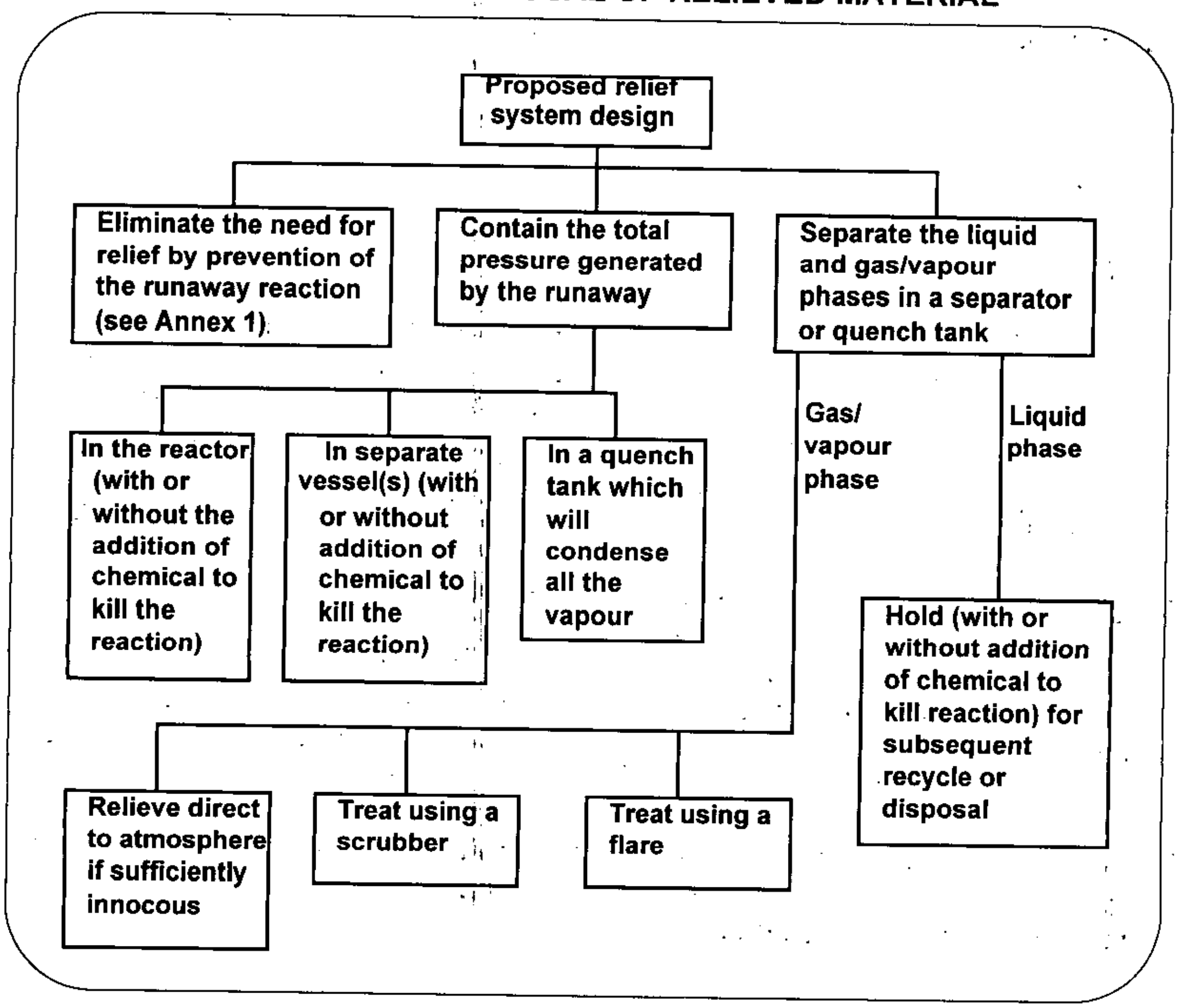
a) Use inherently less polluting processes - this covers both process materials, the design of the process and its control.

b) Dispose of materials which have to be released in ways which minimise harm to the environment. The options are given below.

11.2 OPTIONS FOR SAFE TREATMENT AND DISPOSAL

The options are summarised in Figure 11.1. It is unlikely that all the options given in Figure 11.1 will be viable for any particular reacting system. In some cases (particularly if the material produces a stable foam and/ or is viscous) there can be considerable technical uncertainty in the design of a safe disposal system. In such cases, review of the worst case relief scenario, with a view to preventing it by inherent safety or instrumented protective systems, may be the best option (see Annex 1). It should also be recognised that any liquid/ gas separation system will not be 100% effective and further measures may be necessary to prevent their release to atmosphere.

Figure 11.1 OPTIONS FOR DISPOSAL OF RELIEVED MATERIAL



Containment without any discharge to the atmosphere is one possibility. This may be either in the reactor itself (with a sufficiently high design pressure) or in a separate vessel with top or bottom relief from the reactor to the secondary containment vessel. If containment is not possible, a good strategy is to separate the gas/ vapour phase from the liquid phase. The liquid can then be held for subsequent recycle or disposal, and the gas/ vapour phase can be treated, e.g. by scrubbing or flaring, or vented direct to the atmosphere if sufficiently innocuous.

If necessary, a means of stopping continuing reaction should be built into the disposal system. The two possibilities for this are:

a) Chemical "killing" of the reaction. A suitable chemical may be identified by experimental testing. Adequate mixing of the chemical into the reacting mixture needs to be achieved. This may be easier in a secondary containment vessel, where the momentum of the relief stream can be used to achieve good mixing.

b) Reduction in temperature. This is most usually achieved by quenching.

Where the reaction cannot be stopped; the design needs to take account of the additional heat and gas or vapour generation within the disposal system. For vapour pressure systems, quenching is likely to be a viable option to stop the runaway and to condense all the vapour generated. For gassy systems, the gas will not be removed by quenching and quenching will only be viable if the reacting system will not generate a stable foam when bubbled through the quench liquid (see 4.3). If quenching is not viable, then unless a chemical reaction killer can be identified, considerable gas generation could take place in the disposal system.

Huckins[2] gives advantages and disadvantages of different types of disposal system. This is very useful in the selection of an appropriate system.

The presence of a disposal system may reduce the reliability of the total relief system. For example:

a) The correct level of fluid in a quench tank may not be maintained.

b) Flares may not light.

c) The correct concentration of reacting fluids in a scrubber may not be maintained.

In some cases (e.g. (b) and (c) above), failure of the disposal system will lead to release of untreated hazardous material to atmosphere. In other cases, (e.g. (a) above), failure could lead to overpressurisation of the reactor as well as release of untreated material to the environment. Consideration needs to be given to the effect of the disposal system on the overall reliability and integrity of the relief system. Some limited information on the reliability of relief systems is given by Parry[4].

11.3 DESIGN OF DISPOSAL SYSTEMS

CCPS[1] gives comprehensive guidance on the design of the different types of disposal system. Other useful references are as follows.

11.3.1 Containment systems

Speechley et al.[6] give practical guidance on the design and operation of containment vessels. This topic is also covered briefly by Parry[4].

11.3.2 Separators

Design procedures for vapour/liquid separators are given by DIERS[3], Grossel[7] (which was reproduced by DIERS[3]), API[8] and Singh[5]. Singh also discusses the need to account for level swell of the liquid in a separator.

11.3.3 Quench tanks

This is covered by Huckins[2], DIERS[3]/Grossel[7], Keiter[9] and Singh[5], who also discusses the need to account for level swell in a quench tank.

11.3.4 Flare systems

This is covered by API[8] and Parry[4]. In both cases, the treatment is not specific to the discharge from runaway chemical reactions.

11.3.5 Scrubbers

This is briefly discussed by Parry[4] and DIERS[3]/Grossel[7].

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CHAPTER 12

REACTION FORCES

12.1 INTRODUCTION

Any flow gives rise to reaction forces in the piping and on the vessel supports which may be unbalanced by other reaction forces. The magnitude of these forces may be large (of the order of tonnes force or tens of tonnes force) for emergency relief systems because of the combination of large cross-sectional area and high velocities. The forces therefore need to be evaluated so that adequate support of the piping and vessels can be arranged.

12.2 ESTIMATION OF REACTION FORCES

Figure 12.1 shows the directions of the main steady-state reaction forces for a typical relief system. (There will also be smaller forces due to frictional pressure drop along the pipe). The thrust force, T_F, at a pipe diameter enlargement for choked homogeneous two-phase flow, assuming negligible momentum downstream of the enlargement (an assumption which may slightly overestimate the thrust) is given by DIERS[1] as:

$$\frac{T_F}{A} = F_D\left(G^2\left[\frac{x}{\rho_g} + \frac{(1-x)}{\rho_f}\right] + (P_E - P_a)\right) \qquad (12.1)$$

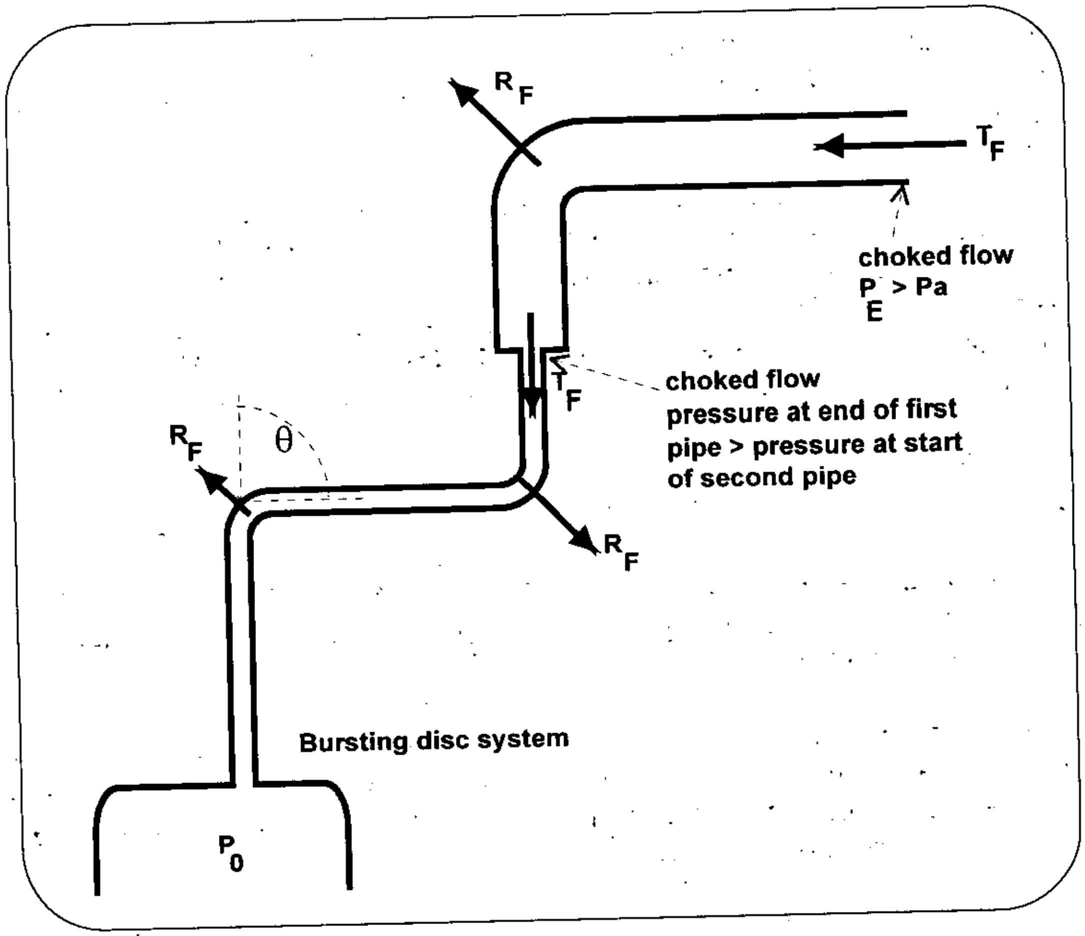
This can be evaluated using the Omega method, if applicable (see Annex 8) or other HEM model (see Annex 4). The Omega method can be used to obtain G and the exit choke pressure, P_E for the upstream pipe. An isenthalpic flash calculation can then be performed from the stagnation pressure at the start of the pipe to the choke pressure, P_E, in order to evaluate the mass fraction of vapour, x, at the pipe exit. If the flow is not choked, then the term (P_E - P_a) becomes zero.

DIERS[1] presented a series of design charts, based on the Omega method, which can be used to evaluate the thrust force. These charts do not include the dynamic load factor, F_D. If a load is suddenly applied, as will be the case following operation of a relief system, the piping will experience a dynamic load of approximately twice the applied load. It is therefore usual to use a dynamic load factor of 2 in equation (12.1). Leung[2] also discusses the use of the Omega method to calculate reaction forces.

The reaction force at a bend is given by:

$$\frac{R_F}{A} = F_D\, 2\sin\left(\frac{\theta}{2}\right)\left(G^2\left[\frac{x}{\rho_g} + \frac{(1-x)}{\rho_f}\right] + (P - P_a)\right) \qquad (12.2)$$

Figure 12.1 DIRECTIONS OF STEADY-STATE REACTION FORCES FOR A TYPICAL RELIEF SYSTEM



It is difficult to use the Omega method to obtain the pressure at a bend, but some estimate can be made knowing the upstream pressure and downstream choke pressure.

DIERS recommended that reaction forces for both the two-phase flow and gas/ vapour-only flow be evaluated because the forces for gas/ vapour flow may be the larger. For the frictionless flow of ideal gas in a constant diameter bursting disc system, the thrust force is given by[3]:

$$\frac{T_F}{A} = F_D\left[(1+k)\left(\frac{2}{1+k}\right)^{\frac{k}{k-1}}P_0 - P_a\right] \qquad (12.3)$$

where P_0 is the stagnation pressure in the upstream vessel.

DIERS[1] gives the following equation for the thrust force due to flow of an ideal gas in a safety valve system:

$$\frac{T_F}{P_0 A_n} = F_D \left[2\left(\frac{2}{1+k}\right)^{\frac{k}{k-1}} - \left(\frac{AP_a}{A_n P_0}\right) \right] \tag{12.4}$$

where A_n is the flow area through the safety valve nozzle and A is the cross-sectional area of the downstream piping. DIERS[1] provides charts which evaluate this equation.

For bursting disc systems, in addition to the force due to steady-state flow (given in equations (12.1) to (12.4)), the force due to the initial unsteady flow should also be considered. It is possible that this can be larger than the steady force if the steady-state flow is limited by friction. Although this force is of very short duration (the time taken for a pressure wave to travel between successive bends), it is important to consider it when designing piping and vessel supports. DIERS[1] gives this force as:

$$\frac{T_F}{A} = F_D(P_0 - P_a) \tag{12.5}$$

In the transient flow case, the duration of the force given by equation (12.5) may be shorter than the natural frequency of the piping, in which case the dynamic load factor will be less than 1[4].

Having evaluated the magnitude of the reaction forces, piping supports should be designed to constrain the piping. The vessel supports also need to be made strong enough. The design of the supports should be such that thermal expansion and contraction of the piping is possible.

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CHAPTER 13

MAINTENANCE OF HARDWARE AND SOFTWARE

13.1 RELIEF DEVICES

Safety valves should be inspected and maintained on a regular basis to ensure that they will operate as required. Bursting discs should also be inspected for build-up of material and damage, and should be replaced at the interval recommended by the manufacturer or a competent person.

The removal of any relief device from a process plant requires a safe system of work such as a written safety procedure and a formal permit to work before the work commences. It is essential that the replacement device is to the correct specification and installed correctly otherwise the integrity of the system will be affected. To this end, it is recommended that the replacement is approved by a competent person who has access to the records of the installation. Further information is given by Parry[1].

13.2 DEVICES WHICH LIMIT THE WORST CASE RELIEF SCENARIO

There are a lot of possible ways in which the worst case relief scenario can be limited. These include:

a) Restriction of flow rate of feeds to prevent/ reduce accumulation of reactants in the reactor.

b) Limitation of the temperature of heating media (however, for semi-batch or continuous reactions, it may be necessary to keep the temperature above a certain level to prevent accumulation of reactants).

c) Special operating procedures and training to ensure that manual additions are of the correct material, in the correct order and of the correct quantity.

d) Use of safety instrumented systems (trips) of sufficient safety integrity (see Annex 1) to prevent runaway reactions which would place a more onerous demand on the pressure relief system than the worst case for which it has been designed.

In all such cases, the adequacy of the relief system depends on the integrity of the method(s) used to limit the worst case. It is important to check regularly that these methods are still in place.

For mechanical systems (e.g. (a) and (b) above), it is important to ensure that, during maintenance, the safety functions of equipment are recognised. Otherwise, they may be replaced with unsuitable equipment. For instance, it is preferable for flow restrictors to use an orifice welded within a short length of pipe, so that it cannot easily be left out, rather than an orifice plate that slips between pipe flanges. It is desirable to have some method of clearly indicating that such equipment has a safety critical function.

The integrity of safety instrumented systems is usually dependent on proof testing at specified intervals (often at a frequency between monthly and three-monthly). Safety management systems[2] need to be in place to ensure this and that any safety critical operating procedures such as described in (c) above are adhered to.

13.3 RELIEF LINES AND DISPOSAL SYSTEMS

It is necessary to ensure the continuing integrity of the whole relief system, including the system pipework, by regularly inspecting for corrosion and soundness of piping supports. It is also necessary to keep relief systems clear from blockages. The relief piping should be designed to prevent ingress of rainwater or, if this is not possible, the system should be provided with drainage and protected against corrosion.

Many types of disposal system need regular maintenance and/or operator intervention to ensure they are available for use when required. Quench tanks should be filled with the correct quantity of quench fluid, and emptied and refilled after any relief event. Scrubbers require pumps to operate correctly, and, in some cases, for an operator to check and adjust the concentration of chemicals within the circulating liquor. Again, good safety management is required.

13.4 DOCUMENTATION

It is important to document the relief system design so that it can be taken into account in any future modifications. The documentation should normally include the following:

a) Details of experimental testing carried out.

b) The basis of safety chosen (see Annex 1) and worst case relief scenario (see Chapter 3).

c) Relief system and disposal system sizing calculations.

d) A statement of the operating envelope for which the installed relief system is adequate.

e) A list of all the safety-critical items of equipment and safety-critical operating procedures, in addition to the relief system itself.

f) A process and instrumentation diagram.

g) Data sheets and specifications for the relief devices and other safety-critical items of equipment.

h) Reference to safety studies such as HAZOP.

13.5 CHANGE MANAGEMENT

It is important that no part of the total relief system (including both the relief system hardware and the chemical reaction system for which the relief system has been designed) is modified without consideration of the safety implications on the overall system. This is facilitated by good documentation, as described above.

Change management is particularly important for multi-purpose reactors. When beginning a new campaign, it will be necessary to check that all modifications required for safe operation of the new reaction have been implemented. This may sometimes include the installation of different relief devices with a new relief pressure.

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