



CHEMICAL INDUSTRIES
ASSOCIATION

Reactor relief venting

Strategic considerations



Responsible Care

Responsible Care

Responsible Care is an international chemical industry voluntary initiative. It is designed not only to improve the performance of the chemical industry in the fields of health, safety, environment, product safety, distribution, emergency response and relations with the public, but also to enable companies to demonstrate that these improvements are in fact taking place. Responsible Care is about continual improvement in performance and communicating with our stakeholders.

Acknowledgement

A working group set up by the CIA's West Yorkshire Responsible Care Cell (WYRCC) prepared this document. Input was also received from members of the CIA's Speciality Chemicals Risk Interest Forum (SCRIF)

The CIA particularly thanks the members of the working group who wrote the document and their companies who generously allowed them time, namely:

G Arthur	Syngenta
S Birkby	Consultant
K Dixon-Jackson	Ciba
C Drew	SORIS/WYRCC
G Hadwen	A H Marks
S Leigh	Croda
C Ludlow	Ciba
K Patterson	Synthomer
I Walker	A H Marks
E Webster	Arch Chemicals
S White	A H Marks

The working group and the CIA would particularly like to thank Yorkshire Chemical Focus for providing funding to support the completion of this document.

© Chemical Industries Association 2006

All rights reserved. Except for normal review purposes, no part of this document may be reproduced, utilised, stored in a retrieval system or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage or retrieval system without written permission of the publisher.

Chemical Industries Association
Kings Buildings, Smith Square, London SW1P 3JJ
Phone: 020 7834 3399 Fax 020 7834 4469
e-mail: publications@cia.org.uk

CIA/0306/BE3/pdf

Table of contents

Foreword	3
1 Venting considerations	4
1.1 Stage 1: New product or process opportunity arises	5
1.1.1 Factors to consider	5
1.1.2 Output	5
1.2 Stage 2: Preliminary safety screen	5
1.2.1 Factors to consider	5
1.2.2 Output	5
1.3 Stage 3: Process development work	6
1.3.1 Factors to consider	6
1.3.2 Output	6
1.4 Stage 4: Screening – Early hazard identification	6
1.4.1 Factors to consider	6
1.4.2 Output	7
1.5 Stage 5: Formal hazard study	7
1.5.1 Details of the hazard study	8
1.5.2 Output	8
1.6 Stage 6: Process risk assessment	8
1.6.1 Output	8
Appendices	
Appendix 1: Examples of possible deviations from normal practice	9
Appendix 2: Reference sources	11
A.2.1: Guidance on methodology	11
A.2.2: Guidance on information sources	11

This document represents a distillation of the views of the authors that others can usefully take into account in their operations.

It does not claim to be a complete and authoritative text, nor best practice, but provides an outline methodology of an acceptable way to operate.

Foreword

Calculating whether a reactor vent is large enough to cope with an emergency is a lengthy process. Repeating the calculations for many different situations is clearly wasteful. On the other hand a company must satisfy itself and the regulatory authorities that it has developed a process for which the associated risks (to people, the environment and property) have been reduced to as low as reasonably practicable, in normal operation and when perturbed.

The West Yorkshire Responsible Care Cell (WYRCC) has prepared an outline methodology to assess the adequacy of the venting strategy chosen by a company. It is intended to help companies reach a robust answer without excessive effort. This document is not a complete and authoritative text, nor does it claim to be best practice. Here is an acceptable way to operate, not the best way. It should guide companies in the handling of the data they possess and direct them towards the gathering of information which they need.

WYRCC advice cannot substitute for a company's expert knowledge of its own processes and the application of its own professional judgement. Companies should consider the specific process, plant and local environmental conditions in all steps, and add to the guidelines suggested if it is warranted. All steps or guidewords included in this document should be considered, and only omitted with justification. It is very strongly recommended that companies keep a written record of each decision step with a note of the outcomes and reasons.

Companies should understand clearly that reactor venting should never be a primary basis of safety and might be inappropriate in some circumstances – for example where environmental damage cannot reasonably be prevented, or it is impossible to vent a material because of its physical properties. Reactor venting should be considered towards the base of any hierarchy of safety measures (i.e. as a near-last resort). Typical measures at the top of the hierarchy include inherent safety measures rather than safety measures that are added on. These can be either inherent in the chemical process itself or inherent in the process plant design measures. Other measures include process control and reaction quenching.

Vents should be used only in specific circumstances and combinations of plant and process. There should be no 'general purpose vents': this line of thought leads to misuse of equipment and potential danger. Where a chemical process is being set up on existing plant, the guidelines can be used to assess the adequacy or otherwise of existing vents, and to assess whether additional measures or a different process or design need to be considered.

1. Venting considerations

The steps needed to determine whether venting is required, and if so, what the venting capacity is, are shown in sequence below. In practice some may be taken in parallel. More importantly the process is iterative – within and between stages. An unsatisfactory output at one stage should prompt reinvestigation of earlier stages, or even terminate a project. Detailed iterations will vary between companies. This document attempts to describe the principles which should be common to all companies.

The job titles given in each step are a suggestion, giving an indication of the level of responsibility or technical expertise required. Individual companies should consider these when applying the guidelines to their own processes and delegating the specific steps.

‘Chemical safety’ and ‘engineering safety’ are used as convenient shorthand for aspects of this analysis. However safety is indivisible: the goal is a combination of product, process and plant which is safe for operators, the environment, customers, neighbours and the site. High safety standards must be achieved whilst maintaining commercial viability. Any conflicts between safety, environmental and commercial considerations should be resolved by considering the process as a whole and repeating some or all of the steps, changing the process and design accordingly. To repeat, companies must satisfy themselves and the regulatory authorities that they have developed processes for which the associated risks (to people, the environment and property) have been reduced to as low as reasonably practicable, in normal operation and when perturbed.

Other safety measures should normally be preferred to venting a reactor and allowing a loss of containment. These will emerge from the steps outlined below: these notes focus on venting alone. Only a small proportion of reactions undertaken by the industry should rely on venting as a Basis of Safety. In the majority of cases venting would be inappropriate because the reaction or decomposition rate is too rapid, because the vented material solidifies immediately in the pipework or for other reasons.

These notes are an aide-memoire. They do not substitute for understanding the chemistry and applying experience.

Regular physical inspection and testing of vents and relief valves (as for all other safety devices) is assumed, but lies outside the scope of these notes.

Investigations into large-scale incidents show, without fail, that no one event or failure is the cause of the incident. Incidents are caused by several co-incidental failures, which can be evident or hidden. In the hazard identification stages it is suggested that two co-incidental failures gives a manageable matrix for consideration, although if one or both of these is hidden, or could be judged to be a common failure, then the scope should be widened.

It is important that the Safety Management Team is a multi-disciplinary team, covering chemistry, chemical engineering, plant operation and management and process safety. Any gaps in knowledge or

experience will lead to the hazard identification process taking longer, as it will raise questions that cannot be answered within the meetings, but have to be given out as actions to people outside the team. However, and more seriously, it could also lead to possible scenarios not being identified. Hazards not identified cannot be tested as potential venting scenarios, nor can the risks be controlled. Therefore an incomplete safety management team will lead to incomplete and less thorough hazard identification, and risks that are neither controlled nor fully mitigated.

1.1 Stage 1: New product or process opportunity arises

Check for environmental and regulatory acceptability considered in a desktop exercise by the business development function with safety, health and environmental (SHE) regulatory input.

1.1.1 Factors to consider

- Outline process development
- Plant fit
- Effluent
- Authorisations
- Export controls
- Cost of production/price of product
- Finance
- Capital spend required?
- Any special factors

1.1.2 Output

A quick and approximate commercial ('Go/No go') decision to satisfy management that there is a reasonable fit between the opportunity and the plant.

1.2 Stage 2: Preliminary safety screen

The Technical Manager should undertake this stage.

1.2.1 Factors to consider

- Synthesis route
- Chemical hazards including any obvious unsafe factors
- Plant availability
- Inherent safety of process

1.2.2 Output

A technical review (from desk and preliminary laboratory studies) to provide a potential route (preferred but not fixed) for which the residual risk is likely to be 'tolerable' and in the 'as low as reasonably practicable' (ALARP) region.

1.3 Stage 3: Process development work

The process development laboratories should undertake this stage.

1.3.1 Factors to consider

- Safety input to process development
- Laboratory safety
- Consideration of effluent treatment and waste disposal

1.3.2 Output

A recommended process (yet to be optimised) for which the residual risk appears ‘tolerable and as low as reasonably practicable’ and with reasonable plant fit. Possible recommendation on using existing plant or building new.

Physical preparation of laboratory samples of product and effluent for analysis or qualification by customers (internal or external).

1.4 Stage 4: Screening – early hazard identification

The safety management team should undertake this stage.

1.4.1 Factors to consider

Consider and investigate the inherent hazards of the process:

- Plant
- Process
- Chemical hazards
- Chemical flows (process flow diagrams)
- Stability/decomposition information and end-points.
[i.e. the identity and properties of materials formed at completion of reaction or decomposition should be known]
- Worst cases
- Containment
- Protection
- Mitigation
- Residual risk
- Tolerability of risk
- ‘What if...?’ explorations of:
 - Heat (including peak temperature, duration of episode, naked flame)
 - Toxicity
 - Gas evolution
 - Pressure increase
 - Flammability
 - Environmental consequences

1.4.2 Output

In parallel with process development, this stage identifies the questions which must be answered. The output from Stage 4 is internal, working information for the company. The questions raised will probably require a literature search and/or laboratory assessment. This may involve small-scale simulations of mal-operations and research from other sources.

1.5 Stage 5: Formal hazard study

This stage provides detailed answers to the questions raised at Stage 4 and should be carried out by the safety management team. It requires a thorough knowledge to be demonstrated of the following factors.

- Normal chemistry
- Deviations from normal operation¹ – identification – consequences – control
 - Credible deviations from normal chemistry
 - Plant, equipment or instrumentation failure
 - Human factors
 - External events, e.g. fire, explosion, flood, hurricane.
 - Deviation assessment – then
- Screen combinations of credible deviations (*likely to trigger venting or pressure relief*)
- Explore consequences for vessel and for downstream plant
 - What happens to the material?
 - Consider gases, steam, foams, vapours, solids, hybrids
 - Vessel/quantity interaction
 - Chemical compatibility
 - Viscosity

Suitable combinations of worst-case consequences to be laboratory tested. Suggested methods include:

 - Phi-tec
 - VSP
 - Adiabatic/low-phi calorimetry
- Quantitative data output used to calculate vent/pressure relief valve (prv) requirements for new plant. Compare them with existing plant provisions!
[If adequate, continue: if inadequate, further iteration of process development needed.]

Some scenarios cannot be modelled in the laboratory, either because the reaction is too rapid, or because the reaction materials are incompatible with the materials of construction of the test equipment, or for other reasons. If this is the case, then companies should seek information from competent sources, or as a worst case, assume that the scenario cannot be vented and make the process safe by other means.

¹ An extended list of situations is in Appendix 1

1.5.1 Details of the hazard study

These notes should be read prior to creating a 'work book' for possible venting scenarios.

Companies must use their own judgement: they should ensure that they have knowledgeable and competent individuals and teams in this area.

1.5.2 Output

- Chemical hazard assessment
 - Data on worst credible scenarios including assumptions and calculations
 - Safe operating envelope definition
 - Environmental considerations and fate of material
 - Chemical basis of safety
 - Plant definition
 - P&ID control system
 - Vent sizes for given combination of process and plant, OR show that venting is not needed, OR that venting would be inappropriate and safe operation is provided in other ways.
- The output will be in a documentary form, which is capable of being shown to regulatory authorities.

1.6 Stage 6: Process risk assessment

These steps are beyond the scope of reactor venting, but are included for the sake of completeness.

1.6.1 Output

- SIL (Safety Integration Level for instrumented safety systems) definition
- Safety shutdown system fixed
- Process basis of safety fixed
- Interlocks and safety measures
- Recheck against known deviations
- Process hazard assessment

Appendix 1: Examples of possible deviations from normal practice

This list is not exhaustive: it is not a comprehensive checklist accurate for all systems but it is intended to provoke deeper thinking about the particular plant and process under consideration. Companies should use their own knowledge of the plant and process to add to the list where it is warranted.

- Temperature too high – (look at +20°C and higher (use judgement)). Is there a runaway point?
- Temperature too low – (look at -20°C and lower (use judgement)).
- Pressure too high – gas, liquid, steam, fire?
- Pressure too low
- Agitation – failure, slow, high, restart after failure, no effect
- Cooling failure
- Heating failure – includes overheating.
- Instrumentation failure
- Vacuum failure
- Other mechanical failure – pumps, valves
- Materials of construction – interaction or failure
- Blockage in reflux line
- Condenser cooling failure
- Wrong result from in-process test
- Reagents/solvents – too much or too little ($\pm 100\%$, $\pm 20\%$, ± 1 unit)
- Catalyst – too much, too little or wrong
- Impurities in reagents
- Wrong concentration
- Wrong sequence
- Wrong time
- Wrong material – previous batch, other materials on plant, similar packaging, similar names, similar numbers, what is connected to vessel? What is in overheads?
- Wrong rate of addition, OR rate of cooling, heating, gas flow – too fast or too slow.
- Wrong storage temperature – too hot or too cold
- Excessive hold time

- Incorrect reaction occurs – unexpected by-products and their consequences on the reaction
- External events – fire, explosion, extreme weather conditions (for example, lightning)
- Failure of connected services – power, water, air or telemetry

Human factors

- Action omitted
- Action repeated
- Too late or too soon
- Right action on wrong target
- Wrong action on right target
- Inappropriate (or no) response to problem or alarm
- Extraneous actions
- Wrong sequence
- Violation of rules and procedures

Appendix 2: Reference sources

The list below provides further sources of information which members of the working group have found useful and which have informed the production of this document. This is not an exhaustive list.

A.2.1 Guidance on methodology

1. 'Emergency relief system using DIERS technology', AIChE/DIERS 1992, ISBN 0 8169 0568 1
2. 'Workbook for chemical reactor relief system sizing', HSE publication, CRR 1998:139, available via the HSE website at www.HSE.gov.uk
3. 'Designing and Operating Safe Chemical and Reaction Processes', HSE guidance book, HSG 143, ISBN 0 7176 1951 9
4. The EU project on Hazard Assessment of Highly Reactive Systems, accessible via the HarsNet website at www.harsnet.de
5. HSE Contract Research Report, 'Safe disposal of vented reacting fluids', CRR100/1996, available via the HSE website at www.HSE.gov.uk
6. 'Reactor pressure relief of fluids containing suspended solids', HSE publication RR 085, available via the HSE website at www.HSE.gov.uk

A.2.2 Guidance on information sources

The following companies are amongst those who can commercially offer guidance and technical support within this area. Again, this is not an exhaustive list and inclusion does not imply endorsement of these companies by the working group, the WYRCC, or the CIA.

1. Chilworth (support and experimental data): www.Chilworth.co.uk
2. HEL (support and experimental data): www.HELgroup.co.uk
3. CIBA Expert Services (support and experimental data): <http://www.cibasc.com/index/exs-index.htm>
4. Burgoynes (support and experimental data): <http://www.burgoynes.co.uk/>
5. ABB Eutech (systems and training courses): www.ABB.com

