1. OVERVIEW

1-1. Prevention of a Major Accidental Release

Prevention of a major accidental release of hazardous materials from a CPI/HPI facility requires proper design, construction to standard, safe operation and management surveillance. An emergency relief system design strategy, which seeks to prevent a major accidental release, should include iterative considerations of hazards and initiating event identification, assessment of risk and mitigation of consequences. Cost effective loss prevention requires an optimizing strategy to prevent, moderate (relieve) and contain a runaway reaction. This iterative three-step assessment approach to emergency relief system design will minimize the potential for unacceptable risk of a major accidental release of hazardous materials to the environment.

1-2. Emergency Relief System Design

Emergency relief system is a multifaceted problem. Of particular significance is whether the relief system must be designed for single or two-phase vapor-liquid flow. Generally, two-phase flow requires a larger relief area than all vapor or subcooled liquid flow. Containment and mitigation of consequences also depend upon a definition of the vapor-liquid phase ratio of the discharged material. Ensuring that an emergency relief system design will either avoid or accommodate two-phase vapor-liquid flow is of particular importance.
2. DESIGN INSTITUTE FOR EMERGENCY RELIEF SYSTEM (DIERS)

2-1. Introduction to DIERS

The Design Institute for Emergency Relief Systems (DIERS), a consortium of 29 companies under the auspices of AIChE (see Appendices i-A and i-B), was formed in 1976 to develop methods for the design of emergency relief systems to handle runaway reactions [1–3]. Of particular interest were the prediction of when two-phase flow venting would occur and the applicability of various two-phase vapor–liquid flashing flow methods for sizing relief systems. DIERS spent approximately $1.6 million to investigate the two-phase vapor–liquid onset/disengagement dynamics and hydrodynamics of emergency relief systems. An overview of the DIERS research program and the significance of the recommended methodology are discussed in this Project Manual.

2-2. DIERS Research Program

The DIERS program evolved over time. The initial focus involved an investigation of two-phase vapor–liquid

- onset/disengagement dynamics,
- relief system hydrodynamics, and
- separate effects experimental verification tests.

The second phase consisted of

- both small- (32-liter) and large-scale (2200-liter) integral blowdown and vented runaway reaction experimental tests,
- computer simulation of the experimental results, and
- technology revisions as required.

The final phase provided

- a design computer program,
- a bench-scale experimental apparatus, and
- an independent review of the basic methodology.

2-3. DIERS Project Manual

This project manual is a record of the DIERS research project. It will help organizations acquire, assimilate, and implement the vast amount of DIERS information and technology by serving as both a reference and training tool. An extensive background and experience are required to properly understand
and apply the information contained herein. Organizations are therefore urged to interpret and use the results through appropriate safety relief specialists.

2-4. DIERS Users Group

Over 75 companies have formed a DIERS Users Group to cooperatively assimilate, implement, maintain, and upgrade the DIERS methodology. Membership is open to industrial or engineering organizations interested in the design, use or manufacture of emergency relief systems or devices [4].

2-5. Availability of DIERS Research Results

The DIERS contractor prepared a series of comprehensive research reports and an emergency relief system design computer program, SAFIRE, which are available from the AIChE Publication Sales Department. An AIChE Continuing Education Course entitled “Emergency Relief System Design Using DIERS Technology” is periodically taught in conjunction with AIChE meetings [4].

3. A STRATEGY FOR MAJOR ACCIDENTAL RELEASE PREVENTION

3-1. Definition

A major accidental release may be described as a fire, toxic emission, or explosion resulting from uncontrolled developments in the course of an industrial activity which leads to serious effects on man or the environment inside or outside the confines of the workplace. The CPI/HPI seeks to prevent a major accidental release from its facilities by

- proper design practice,
- construction to standard,
- safe operation, and
- management surveillance.

3-2. Proper Design Practice

Proper design practices must be employed from the conceptual through the detailed engineering phases. During conceptual design, items such as site selection, plant layout and the concepts of substitution [5] (use less hazardous materials), intensification [5] (use less of a hazardous material) and attenuation [5] (use of a hazardous material at a lower temperature or pressure) are considered. Detailed engineering focuses on preventing potentially hazardous excursions and minimizing the consequences from conceivable releases.
3-3. Construction to Standard

Construction to standard involves utilizing engineering and construction codes and standards and the practices of quality assurance to ensure a well-built facility.

3-4. Safe Operation

Safe operation considers the initial and on-going aspects of day-to-day facility operation. Pre-start-up reviews emphasize

- physical inspection,
- operating and maintenance procedures,
- staff levels and training, and
- emergency procedures and equipment.

Reviews of operating practices and maintenance procedures examine the adequacy of

- daily instructions,
- standard procedures and practices,
- safety rules, and
- training and retraining.

3-5. Management Surveillance

Finally, the management surveillance system should include provisions for

- plant modification approval and implementation,
- periodic safety audits, and
- reporting and responding to hazardous practices and incidents.

4. A STRATEGY FOR EMERGENCY RELIEF SYSTEM DESIGN

4-1. Methodology

Identification of hazards and potential initiating events, assessment of risk and mitigation of consequences are all required to prevent a major accidental release during an emergency relief situation. The processes of identification,
assessment and mitigation are iterative as applied to design of an emergency relief system (Figure i-1).

4-2. Hazard Identification

Hazard identification involves determination of the flammability, toxicity (local and acute, general and chronic), explosibility, and physical properties of materials that are important from an accidental release perspective. Poten-
tial initiating events such as uncontrolled exothermic reaction, design flaws, and human error must be identified.

4-3. Assessment of Risk

Assessment includes consideration of the risk associated with design alternatives, determination of acceptable risk, and steps taken to minimize the potential for unacceptable risk. Differentiation between a worst case and a worst credible scenario is the critical goal. The desirable result is a worst credible scenario with a remote probability and a minor consequence.

4-4. Mitigation of Consequences

Discussion of the mitigation of a major accidental release is beyond the scope of this manual. The consequences of a minor release can usually be mitigated by preparedness as well as safety equipment and emergency procedures.

5. AN APPROACH TO EMERGENCY RELIEF SYSTEM DESIGN ASSESSMENT

5-1. Strategy

The process design should attempt to arrive at an inherently safe facility; that is, one from which a worst-case event cannot cause injury to personnel, damage to equipment, or harm to the environment. This can be achieved through an iterative assessment approach which results in safety features that are intrinsic (built-in), rather than extrinsic (added-on), to the basic design. However, if the technology is not available or is cost prohibitive, a three-step iterative approach can be used to arrive at an acceptable risk at minimum cost through optimization of the measures taken to prevent, moderate (relieve) and contain a runaway reaction or decomposition (Figure i-2).

5-2. Prevention

Many factors must be considered in arriving at the best approach to deal with hazards that may accompany runaway reactions. Thermochemistry, reaction kinetics, thermal stability, process conditions/controls, abnormal operation, contaminants, equipment design, equipment and instrument failures, operating procedures and human error are all examined when evaluating hazard potentials. An approach to the safe design of chemical processes which have the potential for a runaway reaction is to identify and analyze worst credible incident scenarios by proceeding as follows:

- Make an exhaustive search for hazardous conditions by involving
FIGURE i-2. An approach to emergency relief system design assessment.

- Identify the sequences of events which could produce the highest pressure within a vessel and maximum flow from the emergency relief device(s).
- Scrutinize various failure modes to arrive at the combination which produces the worst credible incident scenario.
- Then, utilize reaction, control, process and safety engineering design technologies to prevent, moderate (relieve) and contain runaway reactions.
Design and operating strategies that will help to prevent runaway reactions include

- acquisition of data to identify potential problems;
- measurement and control of critical parameters (temperature, pressure, feed rate, coolant flow, catalyst level);
- operation at conditions (temperature, pressure, concentration) that provide a safe margin from runaway conditions;
- installation of redundant instrumentation to increase reliability of measurement and control of critical parameters;
- use of alarms to warn operators that a critical parameter has changed from its normal condition;
- training to enable operators to safely react to upset conditions;
- automatic emergency shutdown when a critical parameter has deviated from normal by a predetermined amount; and
- prevention of contamination by proper design and operating procedures.

These and many other steps ensure that a runaway reaction will not occur as the result of a single failure.

Finally, the analysis of the likelihood and consequences of multiple failures leads to the identification of the worst credible runaway reaction incident scenario. An emergency relief system can then be designed to handle this incident to include safe disposal of the discharged fluid.

5-3. Moderation (Relief)

Techniques for sizing an emergency relief system for runaway reaction include

- graphic or analytical design methods,
- direct scaling of experimental data obtained in vessels with a very low thermal inertia, and
- computer simulation of incidents and flow through relief systems.

The technique selected depends on the

- Type and number of chemicals involved.
- Availability of required process and experimental data.
- Constraints imposed upon the designer.
In addition to moderation of a runaway reaction by proper sizing of emergency relief, consideration should also be given to installation of a liquid dump system, provision for emergency blowdown of pressure, or use of a "kill" agent.

5-4. Containment

Containment can be approached in two ways. First, vessels may be designed to withstand the maximum pressure that can develop from an upset. Although this approach may be viable for some emergencies, such as a vapor phase deflagration, it may not be a feasible alternative for a runaway reaction or vessel fire exposure because of the extremely high pressure that can be produced.

Second, the term "containment" may also be used to describe the disposal/decontamination of the discharge from a relief system. Vent stacks, vapor-liquid separators, quench tanks, scrubbers, flares, incinerators, or combiners thereof may be used to disperse, quench, scrub, detoxify, or burn the discharged fluid. Aspects of containment are discussed in Chapter V, "Containment, Disposal, and Mechanical Design."

6. TWO-PHASE VAPOR-LIQUID FLOW

6-1. Emergency Relief System Design

Emergency relief system design is a multifaceted problem. Of particular significance is whether the relief system must be designed for a single phase (vapor or liquid) or two-phase vapor-liquid flow. During a runaway reaction, the vessel pressure is affected by the volumetric discharge rate of the emergency relief system and the influence of temperature, composition and mass loss on the reaction rate. If two-phase flow occurs, the volumetric discharge rate, the system mass loss and evaporative cooling effects will be affected by the vapor-liquid phase ratio. Generally, two-phase flow requires a larger relief area than all vapor or subcooled (non-flashing) liquid flow.

6-2. Containment and Mitigation

Containment and mitigation requirements also depend upon a definition of the vapor-liquid phase ratio of the discharged material. Ensuring that the total emergency relief system design will accommodate two-phase vapor-liquid flow is of particular importance.
7. TWO-PHASE VAPOR–LIQUID FLOW ONSET AND DISENGAGEMENT

7-1. Liquid Swell

The surface of a boiling or gas-sparged liquid can rise to the level of a top-mounted emergency relief device if enough bubbles accumulate (i.e., are held up) in a vessel. Gas holdup can be high at low relief rates if the liquid is highly viscous or foamy. Nonviscous, nonfoamy liquids will also swell at high relief rates.

Boiling due to an exothermic or gas-generating reaction takes place throughout the volume of liquid, rather than solely at the surface. Each bubble occupies volume and displaces the liquid surface upward. Individual bubbles are able to rise (slip) through the liquid with a velocity that is dependent on the buoyancy and surface tension and retarded by viscosity and the foamy character of the fluid. If a sufficient volume of bubbles become trapped, the liquid surface reaches the height of the relief device and two-phase flow occurs.

7-2. Two-Phase Blowdown Example

An example should serve to illustrate the phenomenon. A 2-inch diameter relief device (nozzle) was rapidly opened on a tank that was 95% filled with 550 gallons of city water at approximately 150°C and under its own vapor pressure of about 58.5 psig. Approximately 28% of the tank contents vented by two-phase flow (Figure i-3). The experiment was repeated, except that
1000 ppm of a liquid household detergent were added. Approximately 96% of the tank contents vented by two-phase flow (Figure i-4).

Clearly, the foamy nature of the second fluid significantly influenced the character of the two-phase blowdown tests. The DIERS large-scale experiments are fully discussed in Chapter III, "DIERS Phase III Large-Scale Integral Tests."

7-3. DIERS Calculation Methodology for Two-Phase Flow Onset and Disengagement

DIERS developed and tested a method to calculate the onset (start) and disengagement (stop) of two-phase vapor-liquid flow from a vessel due to overpressure relief or depressurization [6]. A first-order lumped-parameter "drift flux" formulation [7] was utilized as a basis for a vapor holdup correlation. An empirical parameter $C_0$ was used to adjust the correlating relationships to available data. Vapor holdup in a vessel is influenced by axial and radial effects created by a two-phase boundary layer due to an external heat flux [6,8], internal circulation [6,8] and hydrostatic head. Calculation methods for two-phase flow onset and disengagement are discussed in Chapter I, "Vapor Disengagement Dynamics."

8. TWO-PHASE VAPOR–LIQUID HYDRODYNAMICS

8-1. Two-Phase Flow Models

DIERS examined various two-phase vapor–liquid flow models from the open literature [9] and tested them using an overall system model against large-

8-2. Homogeneous-Equilibrium Flow

Two-phase vapor–liquid homogeneous-equilibrium flashing flow proved to be the most conservative model for estimates of flow capacity from both safety valves and rupture disks. However, this model is not sufficiently conservative for safety valve back pressure calculations or effluent containment considerations because under certain circumstances the appropriate application of other models will predict higher flow rates.

9. DIERS BENCH-SCALE APPARATUS

9-1. Experimental Data for Emergency Relief System Design

A careful experimental program that uses representative samples is required to obtain data needed as a basis for emergency relief system design. The present state of experimental development should be considered when selecting an apparatus to acquire data.

9-2. Functions of the DIERS Bench-Scale Apparatus

DIERS sponsored the development of a bench-scale apparatus and a low thermal inertia test cell that can be used to provide thermal stability and runaway reaction kinetic data [13,14]. The low thermal inertia essentially overcomes a limitation of other commercial devices, namely understating the magnitude of the self-heat rate and the adiabatic temperature rise. For the first time, runaway reactions in the laboratory can approximate the severity of those in industrial vessels. This behavior is extremely useful for the required validation [15] of a computerized runaway reaction model.

This apparatus can also be used to

- differentiate between materials that exhibit homogeneous versus non-foamy behavior during emergency relief by measurement of the final void fraction in a test cell [13],
- compare a measured to a calculated homogeneous-equilibrium flashing mass flux to determine where turbulent (nonviscous) or laminar (viscous) flow exists during a venting incident [13],
• measure parameters required for graphical or analytical methods for emergency relief device design [13], and
• size emergency relief devices directly by using top- or bottom-vented experiments [16,17].

Use of the DIERS bench-scale apparatus is discussed in Chapter VI, "DIERS Bench-Scale Apparatus."

10. RUNAWAY REACTION EMERGENCY RELIEF SYSTEM DESIGN COMPUTER PROGRAM

10-1. Emergency Relief System Design

Emergency relief system design seeks to prevent a major accidental release through the following means:

• Identification of hazards and potential initiating events.
• Assessment of risk by consideration of alternative methods of prevention, moderation (relief), and containment.
• Mitigation of consequences.

Use of adiabatic runaway reaction test information in combination with digital simulation is a powerful method to design an emergency relief system when consideration of alternatives is required.

10-2. Digital Simulation

Mathematical modeling using digital simulation allows quantification of rates of heat release and pressure and temperature changes for a variety of operating and upset conditions. Design possibilities can be examined by exploring the following alternatives:

Prevention
• Concentration
• Operating temperature
• Catalyst concentration
• Feed rate
• Alarm/shutdown setpoints
• Cooling capacity under upset conditions
• Contamination
• Heat losses
• Fire exposure heat flux (insulation, water spray)
• Fire exposure duration
Moderation (relief)

- Safety valve versus rupture disk
- Relief device set pressure
- Staggered relief pressures
- Vessel fill ratio
- Top- versus bottom-mounted relief devices
- Use of volatile solvents

Containment

- Vessel MAWP
- Vent stacks (dispersion)
- Vapor–liquid separators
- Quench tanks
- Scrubbers
- Flares
- Incinerators

Combinations of these and other factors determine the emergency relief system design basis.

Digital simulation helps to promote a focus on prevention of a runaway reaction and determination of the worst credible scenario. Once a validated model is in place, simulation allows parametric studies that improve our assessment of risk. Simulation also allows a ready examination of the effects of several partial-disengagement and two-phase flow models on emergency relief and containment system designs.

Use of digital simulation does require a comprehensive computational capability. When the limitations of alternative methods are understood and the cost and performance advantages of an optimal combination of prevention, moderation (relief) and containment of a runaway reaction are appreciated, rigorous computer simulation may be the preferred course of action.

The nonlinear heat and mass balance differential equations, which describe the transients of a worst credible runaway reaction incident, and the fluid dynamic equations, which describe the flow capacity of an emergency relief system, are normally solved by numerical integration in a digital simulation computer program. The kinetics, stoichiometry, heats of reaction, physical properties, and vapor–liquid equilibrium constants for the materials present are read into the computer program from a data file. All properties should be a function of temperature in accordance with recognized thermodynamic models.

Program input and output describing the physical situation should be checked for consistency and printed to provide a written record of the calculations. The mass of each component should also be continually checked to ensure a balance. A variable time-step controlled by the rates of tempera-
ture and pressure changes may be used to maintain numerical accuracy for stiff (rapid runaway reaction) systems. Warning messages are usually provided if the emergency relief devices cannot maintain the system pressure to meet ASME pressure vessel code requirements.

10-3. History of Emergency Relief System Design Computer Program Development

Huff appears to have been the first [18] to publish a computer simulation method to size emergency relief devices. His model introduced the "uniform froth" or "homogeneous" concept to allow simulation of two-phase venting. A slip-equilibrium hydrodynamics model for relief system flow was also documented.

Huff subsequently [19,20] refined and extended his simulation program to cover the disengagement range from all vapor to all liquid relief. Additional two-phase hydrodynamic details were provided.

Huff has summarized [21] the basic method and equations in his versatile program and illustrated the use of previously published DIERS disengagement (churn-turbulent) and hydrodynamic (homogeneous-equilibrium) models. Versions of this computer program were kept current with DIERS findings and have contributed greatly to an understanding of the DIERS experimental data over the years.

10-4. SAFIRE Computer Program

Two of the DIERS contractors also developed computer programs. Fauske & Associates, Inc. [22, 23] developed an extremely versatile program which describes the multi-phase dynamics for emergency relief of a batch chemical reactor or storage vessel. All of the DIERS analytical methods were incorporated into the code. The program that resulted (SAFIRE) was used to analyze the two-phase vapor-liquid relief from the DIERS sponsored large-scale runaway reaction and blowdown experiments. SAFIRE models vessel transients using a lumped-parameter approach by assuming averaged temperature, pressure and phase compositions exist throughout the vessel. Vent pipe flow is assumed to adjust instantly to changes in stagnation conditions at the vessel outlet. The steady state flow equations are numerically integrated over the length of the relief device. This computer program was distributed to DIERS members and has recently been made available for sale to non-DIERS members by the AIChE DIERS Users Group. A description of the computer program is discussed in Chapter VII, "SAFIRE Computer Program for Emergency Relief Sizing."
10-5. DEERS Computer Program

JAYCOR [24] independently developed a one-dimensional computer program, called DEERS, for relief of runaway reactions. This program solves the Navier–Stokes equations in space and time for the mass, momentum, and energy balance equations of the vapor–liquid mixture as well as an equation for the relative motion between the vapor and liquid. The JAYCOR program models local transients over the height of the vessel and length of the vent piping by calculating the propagation of changes (pressure, liquid holdup, etc.) from point to point in the vessel and relief system. This program and a “two-fluid model” were also successfully used to analyze the DIERS large-scale tests. The program is suitable for design of relief systems for runaway reactions and is available for sale/license to the CPI/HPI. Use of and results from the DEERS computer program are discussed in Chapter I, “Vapor Disengagement Dynamics.”

11. REFERENCES

### APPENDIX i-A. DIERS Committees

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APPENDIX i-B. DIERS Sponsors

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