

Designing Emergency Relief Systems for Runaway Reactions

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This guidance applies to reactive systems subject to process- and fire-induced runaway reactions, tanks that store reactive materials, and two-phase flow of reactive materials.

Do you suffer from the ERS design ostrich syndrome? Most companies are well-equipped to perform emergency relief system (ERS) design for single-phase flow and non-reactive systems. Existing standards and recommended engineering practices developed by organizations such as the American Society of Mechanical Engineers (ASME), National Fire Protection Association (NFPA), American Petroleum Institute (API) and AIChE's Center for Chemical Process Safety (CCPS) enable a competent engineer with proper training to perform such calculations with a high degree of confidence and accuracy.

Reactive systems, however, are more complex, and may be susceptible to fire-induced and process-induced runaway reactions. The reactive characteristics of the material should be well understood by the ERS designer, including the material's potential to react with itself, decompose, rearrange or react

with any contaminants present, such as water, air, rust, etc. All reactions that could occur should be identified and the kinetics of these reactions determined, either by experiment or through trusted literature sources. And, the characteristics of the vessel contents must be known so that two-phase flow methods may be utilized as appropriate.

The possibility for runaway reactions should be considered for all reactive chemicals. Keep in mind that while a material may not be reactive at normal operating conditions, it might be at relief conditions, depending on the setpoint of the relief device, the nature of the vessel contents (*e.g.*, foamy vs. non-foamy), contamination, composition and flow regime. To ignore the potential for runaway reaction, or to simply state that a runaway reaction is not credible, is irresponsible, extremely risky, and potentially very hazardous. If analysis shows that a runaway reaction is not credible, the rationale

Practices, Standards and Regulations

Conflicts among federal regulations and recommended practices, codes and guidelines issued by different organizations are not uncommon. When faced with such conflicts, the designer should, at a minimum, meet or exceed the requirements of the Occupational Safety and Health Administration's (OSHA) Process Safety Management (PSM) (1) and Environmental Protection Agency's (EPA) Risk Management Program (RMP) (2) regulations. When the consensus codes conflict, the guidance that provides the most conservative design should be used. AIChE publishes extensively on relief system design through CCPS (3–5) and the Design Institute for Emergency Relief Systems (DIERS) and DIERS Users Group (6).

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Screening for Reactivity

Numerous theoretical, computational and experimental tools can be used to screen for reactivity (1–5).

Theoretical and computational screening checks include: material safety data sheets (MSDSs); supplier-recommended storage and handling practices; physical property and hazard data; chemical incompatibility matrices; published and online reactivity data sources, such as Bretherick's (6) and NFPA hazard ratings; incident data from facilities handling materials with similar chemical structures and molecular bonds; formation energies; heats of reactions (e.g., polymerization, decomposition, solution); computed adiabatic reaction temperatures (CART); and oxygen balances.

Software tools that aid in reactivity screening include: the National Oceanographic and Atmospheric Administration (NOAA) web-based chemical-interaction matrix utility (7), the National Aeronautics and Space Administration's (NASA) CET93 (8), the National Institute of Standards and Technology's (NIST) SP program (9), ASTM's CHETAH (10), SuperChems Reactivity Expert (11), and others.

Experimental tools include: the blasting cap test; flame test; gram-scale heating test; drop weight test; thermogravimetric analysis (TGA); differential thermal analysis (DTA); reactive systems screening tools (RSSTs); and differential scanning calorimetry (DSC).

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behind this conclusion must be well-documented.

Discounting such scenarios without proper justification exposes your facility to extreme risk. Doing so is a sign that you are suffering from the ERS design ostrich syndrome.

The power of negative thinking

Look for scenarios of what can go wrong. Federal regulations, codes, and recognized and generally accepted good engineering practices require that the pressure-relief system be sized for the worst credible over-pressurization scenario (1–3).

To identify the worst-case scenario, first identify all possi-

ble over-pressurization scenarios. A good starting point is the most recent hazard and operability (HAZOP) study. A well-executed HAZOP study will have identified the equipment, administrative and human failures that can lead to over-pressurization of the vessel and potential loss of containment.

Ensure that all potential over-pressurization scenarios were, in fact, identified by the HAZOP team. This requires reviewing:

- the information pertaining to the hazards of the chemicals in the vessel (or chemicals that could be present under abnormal operations), including interactions with contaminants (e.g., rust, water, oxygen, chemical impurities, etc.)
- the information about the chemistry of the process and possible reactions, including self-reactions, polymerizations, decompositions and rearrangements, and the effects of contaminants on these reactions
- the piping and instrumentation diagrams (P&IDs) for the vessel and associated equipment
- the equipment drawings to determine volumes, surface areas, materials of construction, instrument ranges and alarm/interlock setpoints, etc.

Armed with this information and the HAZOP study, determine what can go wrong. This requires intense brainstorming. A good reference for starting the brainstorming process is API 521 (4), which lists common causes of overpressure and design considerations. Safeguarding Memorandum (SGM) is another established scenario-identification technique. Be cautious, however — only the AIChE Design Institute for Emergency Relief Systems (DIERS) methodology is widely recognized for sizing relief devices for reactive service.

Determine the potential for a runaway reaction by carefully scrutinizing the information available. If the vessel contains reactive chemicals, a runaway reaction, in particular if fire-induced, will probably be the worst-case scenario. Be especially cautious of any material that: has an NFPA instability rating of 1 or higher (5); that is identified as reactive; or that has reactive properties listed on its material safety data sheet (MSDS).

Think negative. Think of everything that can go wrong.

It's all about the chemistry

Reactive systems are not forgiving. Exothermic reactions generate heat, which causes the temperature in the vessel to rise. Typically, a reaction rate doubles with every 10°C temperature rise. If there is insufficient cooling, these phenomena lead to an exponential increase in temperature and pressure — an uncontrollable runaway reaction.

The importance of understanding the reaction kinetics cannot be overemphasized. It often means the difference between adequately venting a reaction and an uncontrolled runaway.

Reactive chemistry is challenging, because reaction rates are sensitive to temperature, contamination, interactions, and more. For example, ppm levels of a contaminant can change

the flow behavior of a system from non-foamy to foamy, which has a significant impact on the size of the required relief device. Furthermore, it can catalyze the reaction, or react with materials present to form a catalyst that can greatly accelerate reaction rates. These catalysts can also lower the temperature at which the reaction rates become significant, which can make an otherwise non-credible runaway reaction become credible.

Because of the complexity of the reaction dynamics and the reaction rate's dependence on temperature and concentration, it is rarely possible to design a proper relief system involving runaway reaction without dynamic simulation tools and/or adiabatic calorimetry testing.

Fire-induced runaway reactions

If a facility stores or handles large quantities of flammable materials onsite, especially if they are above their flash point, fire is a credible scenario, and a fire-induced runaway reaction should be considered. Relief requirements for fire-induced runaways are almost always larger than relief requirements for a process-induced runaway. A fire causes the temperature of a reactive material to reach the onset of a runaway with little reactant consumption. This leaves more reactant to react and generate heat and pressure. The impact of this additional heating on reaction rates is exponential. Many commercial systems (such as monomers) are stored with inhibitors. Fire exposure can deplete the inhibitor, and when this happens, the runaway reaction can proceed at a much higher rate than the rate at the runaway onset temperature.

A properly designed relief device protects against overpressure, but not necessarily overtemperature. A long-duration fire or flame jet impinging on a localized area of the vessel will ultimately weaken the structural integrity of the vessel, causing it to fail. Deluge systems and/or fireproof insulation are often used in conjunction with relief devices for reactive materials to reduce the impact of fire and to obtain reasonable relief.

The fire flux is an extremely important design variable for a reactive system. Common formulas for calculating fire heat input to the vessel can be obtained from API 520 and 521 (2–4), NFPA-30 (6), and OSHA 1910.106 (7). Unfortunately, the API and NFPA-30 fire formulas do not agree on the value of the fire flux, NFPA-30 being more conservative than API-520/521 (up to a wetted area of 2,800 ft²). The OSHA standard uses the NFPA-30 formulas.

In addition, OSHA issued three interpretation letters on this subject (7). For aboveground storage vessels containing a PSM-regulated material, the OSHA formulas for fire flux and insulation credit should be used.

Fire researchers have experimentally measured the flame emissive power and fire flux of many hydrocarbon fuels from pool fires and flame jets, as well as burning rates and flame length/height correlations. For many fuels, it is possible to

Obtaining Calorimetry Data for ERS Design

Adiabatic calorimetry is an important tool that is widely used to quantify and understand the potential hazards of runaway reactions under adiabatic conditions. The Accelerating Rate Calorimeter (ARC) and Automated Pressure Tracking Adiabatic Calorimeter (APTAC) by TIAX, LLC, and EuroARC from Thermal Hazard Technology are used by many companies and ERS consultants around the world to collect the thermo-kinetic data under near-adiabatic conditions required to size relief devices for reactive systems. The Reaction Calorimeter (RC1) from Mettler-Toledo is also used (with caution) to obtain heats of reaction data and to simulate actual reaction processes on a 1-L scale. Vent sizing instruments, such as the Advanced Reactive Systems Screening Tool (ARSST) and the Vent Sizing Package (VSP2) from Fauske and Associates, Inc., and PHI-TEC from Hazard Evaluation Laboratories (HEL), are also useful.

obtain a good fuel-specific estimate of burning rates (fire duration), flame height and fire flux (heat input).

The fire heat input used for design should meet or exceed the OSHA standard (where it applies).

For vessels containing reactive liquids or non-reactive liquids known to be foamers, or where two-phase flow is possible due to the disengagement characteristics of the vessel/relief system, use the total surface area of the vessel as the wetted surface area when estimating the heat input to the vessel. API and NFPA-30 guidelines ignore the impact of two-phase flow on the selection of wetted area and can lead to non-conservative designs. This effect must be established using advanced simulation techniques, such as those embodied in SuperChems Expert and SuperChems for DIERS.

For vertical vessels, at a minimum, the first 30 ft of elevation above grade should be considered as being exposed to the flame from a pool fire in order to comply with OSHA 1910.106 and NFPA-30. (API considers only the first 25 ft to be exposed.) However, pool fires actually produce flames that may be hundreds of feet high, and many prudent engineers assume that the entire vessel, regardless of height, will be exposed to the flame from a pool fire.

Insulating reactive-chemical storage tanks

Insulation is commonly used to minimize heat input to a vessel when it is exposed to a fire (8). However, the insulation will also minimize heat loss from the vessel during a runaway reaction. In the case of fire exposure, the insulation will prevent the vessel contents from cooling after the fire is put out, and this may lead to a runaway reaction.

If insulation is used, consider how the vessel contents can be drained, cooled, inhibited or used in the process before the reaction starts to run away. In most cases, there will be many uncertainties: Has the fire destroyed the equipment, instrumentation and power supplies needed to accomplish these tasks? Is there a concern about the integrity of the structures and equipment that would have to be used? Will the investigating agencies (fire marshal, OSHA, Chemical Safety

Thermal Inertia: Friend or Foe?

This question is highly debated by calorimeter vendors. In fact, thermal inertia is more of a friend than a foe.

Thermal inertia is a measure of the thermal capacity of the test cell plus the contained sample compared to the thermal capacity of the sample itself. Thermal capacity is defined as the heat capacity of the material (Btu/lb-°F) multiplied by the mass of material present (lb). The value obtained is the amount of heat required to raise the temperature of the material 1°F.

A very large plant-scale vessel will have a thermal inertia close to 1, *i.e.*, the vessel's thermal capacity is small compared to the material's thermal capacity. This is especially true during a runaway reaction, when the temperature of the reaction mass is rising very rapidly and the rate of heat transfer to the vessel is insufficient to allow the vessel temperature to rise at the same rate.

An indication of high thermal inertia can mask weak reactions or precursors to dangerous reactions, which may be secondary or tertiary exotherms. But for many fast reactions involving polymers, it is very helpful to know the thermal inertia, because one can capture the entire reaction process before the test cell ruptures.

If calorimeters with high thermal inertia are used, ensure that the reaction selectivity does not change with thermal inertia. Run duplicate experiments at different thermal inertia values. Tools like SuperChems for DIERS and SuperChems Expert allow for easy scale-up of this fundamental thermo-kinetic data from high thermal inertia to a thermal inertia of 1 or to the actual thermal inertia of the vessel.

Review Board) permit entry into the area? Because of these unknowns, deluge systems should also be considered.

If vessels containing reactive chemicals must be insulated, a clear understanding of the runaway reaction's characteristics should be obtained from adiabatic calorimetry data. Use proven dynamic-simulation computer codes to establish the required relief capacity, the time to maximum rate, and the required response time for corrective actions for the proposed insulation thickness.

Sizing for two-phase venting

For polymer systems, systems sensitive to peroxidation, systems in dirty service, known foamers, and the like, assume foamy behavior. For many gassy or hybrid systems, all-vapor flow should be considered, because active ingredients may be concentrated during all-vapor venting, which leads to a more dangerous situation.

When faced with uncertainties caused by the use of complex methods or limited data, select the conservative design basis. Also weigh the advantage of expending resources to reduce uncertainties and complexities to an acceptable level vs. the cost advantage of a simpler, but conservative, design basis.

High-viscosity two-phase venting

High-viscosity two-phase venting occurs in many industrial-scale reactors handling polymer systems (9). For example, a runaway reaction in a monomer tank produces viscous poly-

mers that can lead to high-viscosity two-phase flow, which must be vented through the reactor's emergency relief system.

Many polymerization reactors are equipped with relief devices with discharge lines that are 50–100 ft long (or longer). Discharge lines are typically connected to a vent containment header and/or a flare header. Many existing relief systems were designed using best industry practices, such as API-520. A recent study found that 33% of the 14,873 pressure relief devices examined had excessive inlet pressure drop and 49% had excessive outlet pressure drop (10). These studies were based on work done by companies to comply with the OSHA PSM rule, which requires verification that the relief device design and design basis have been appropriately evaluated and documented.

What is alarming is that these numbers refer to relief devices that were incorrectly sized for all-liquid or all-vapor flow for low-viscosity systems. The presence of a two-phase discharge introduces many complications — one must deal with a fluid system that has the density of a liquid and the compressibility of a gas.

Several attempts have been made to hone best industry practices so that simple techniques could be used to obtain a better estimate of a safe design. Until recently, a widely accepted method of designing a relief system for high-viscosity two-phase flow did not exist. To address this shortcoming, the DIERS Users Group sponsored three research projects in this area and recently released SuperChems for DIERS, which includes consensus-based techniques.

Some of the issues involved in designing for high-viscosity two-phase venting include:

- How does one calculate a two-phase viscosity for estimating two-phase pressure drop in the inlet and outlet lines?
- Is there a two-phase-flow Reynolds's number and how is it computed?
- The choke point for a two-phase mixture is influenced by quality and viscosity. How are the vapor quality and associated pressure drop estimated at the right location?
- Does a high-viscosity two-phase mixture separate in the relief valve or in the discharge pipe?
- How sensitive is the final design to small changes in inlet vapor quality?

The issue of calculating a two-phase viscosity is at the heart of the problem. Several publications have suggested that a volume-averaged viscosity should be used; some assigned weighting factors to the vapor and liquid portions of the flow.

A key finding by DIERS is that a high-viscosity two-phase discharge will separate in the discharge line. This is important, because slip flow may lead to a higher pressure drop in the discharge line. Preliminary findings suggest that short discharge lines can be undersized by one to two pipe sizes if the pressure drops were estimated assuming no slip. This increased backpressure can lead to valve chatter and inadequate venting capacities.

The same logic applies to the inlet line if the inlet quality is greater than zero. The allowable inlet pressure drop is restricted to 3% of the pressure relief valve's set pressure. The introduction of slip in the inlet line for non-viscous systems may result in higher pressure drops and larger inlet-line size requirements. Higher-viscosity systems will exhibit more slip, and as a result even higher pressure drops.

Another key finding is that high-viscosity two-phase flow through relief valves is best represented using a homogeneous-equilibrium (no slip) model of flow and viscosity. A two-phase mixture entering the nozzle of a relief valve strikes the disc surface and changes direction by 90 deg. At the disc surface, the fluid's upward velocity should be near zero. In effect, the flow is being arrested by the disc and is established again as the fluid leaves the valve nozzle and enters the body bowl.

High-viscosity two-phase flow velocities are lower than low-viscosity two-phase flows because larger piping and relief devices are required. This leads to longer residence times in the valve throat and, as a result, homogeneous-equilibrium two-phase flow is likely to be established in less than 4 in.

Finally, a homogeneous-equilibrium high-viscosity two-phase-flow model gives predictions for low-viscosity flow that agree with low-viscosity experimental data, as well as predictions for high-viscosity flow that agree with the limited data collected for those conditions.

Other over-pressurization safeguards

A relief system offers only one layer of protection against a runaway reaction. When dealing with reactive chemicals, additional layers of protection should be provided to reduce the likelihood of a runaway reaction to a non-credible level, and to increase the total system reliability beyond that of the pressure relief devices alone.

The reliability of pressure relief devices is only fair at best. In one study of 13,000 relief valves, 18% opened at more than 110% of their set pressure; another 3% didn't open at all (11). When the consequences of relief-device failure are high, this level of reliability is not acceptable.

In addition to mechanical failure, relief valves can also become fouled with solids from the vessel, crystallization products, polymers and remnants of a burst rupture disk installed below it. These foreign materials can restrict the flow through the relief valve, or plug it completely. In either case, the relief device may not be able to handle the flow required to protect against a runaway reaction. For many reactive systems, it is necessary to install two independent relief devices, each sized for the full required capacity. It is also common to provide a flush or purge of the line leading to the relief devices to minimize the potential for fouling.

Reactive systems require, at a minimum, temperature and pressure monitors with displays in the control room and high

Tools for Designing ERSs for Reactive Systems

If you are interested in ERS design for reactive systems and you know the reaction stoichiometry and kinetic data, look into SuperChems for DIERS, a subset of SuperChems Expert marketed by AIChE. If such data need to be reduced from experimental measurements and the stoichiometry needs to be determined as well, an upgrade to SuperChems Expert would be warranted. SuperChems Expert also offers the ability to design effluent handling systems and process headers.

Details on SuperChems for DIERS can be found at www.iomosaic.com/diersweb/htdocs/software/software.html.

and high-high alarms. These instruments will add two layers of protection if they have sufficient reliability. Many companies consider a high alarm plus a high-high alarm as one additional level of protection if they are based on the same field instrument, and only if the operator can effect a change once the alarm is recognized.

Since the consequences are typically severe, it is usually necessary to provide redundant temperature and pressure (Safety Integrity Level [SIL] 2 or 3) instrumentation to obtain the required reliability. For example, when three temperature sensors of different designs are installed to avoid the common mode failure, the control computer can determine which one is in error through a voting system and an established deviation tolerance. The alarms from these instruments will alert the operator that immediate corrective actions are needed.

It is sometimes necessary to have the high-high alarm activate an interlock that automatically takes corrective actions. The automatic interlock eliminates the elements of human error and unavailability/inability of the operator to respond immediately. The interlocks are typically designed to slow or stop the runaway reaction by injecting a poison or inhibitor, injecting an inert solvent to cool the reaction mass, or dumping the reaction mass into a tank containing an inert solvent to cool it. Inhibitor injection is most efficient when the vessel is agitated and the inhibitor can be mixed in with the reactants. Injecting an inert solvent into the vessel, or mixing the reaction mass with an inert solvent in a second vessel, cools the reaction mass and minimizes the potential for overwhelming the pressure relief devices.

When it is not practical to size an ERS for a specific scenario

If the required relief device for a runaway reaction is too large to be practical, additional layers of protection must be provided to prevent the runaway reaction from occurring. This is determined through layer of protection analysis (LOPA).

Do not simply size the device for the next-worst-case scenario. Rather, provide engineering controls that will reduce the likelihood of the worst-case runaway reaction to such a low value that it can be considered non-credible, and design for that new worst-case scenario.

This is achieved by equipping the vessel with addi-

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tional layers of protection that will prevent the runaway reaction from occurring or mitigate it if it starts. The number of layers of protection should be determined by performing a risk assessment that considers everything that can go wrong and what actions can be taken to prevent or mitigate the runaway reaction. ASME Code Case 2211 (12), CCPS (13–15), and Melhem and Stickles (16) provide guidance on performing such risk assessments. The objective is to obtain sufficient layers of protection so that the likelihood of the runaway reaction meets the corporate guideline required to discount this scenario, typically 10^{-6} years.

Instrumentation with SIL 2 or 3 performance must be provided to ensure reliability. Guidance on the system requirements to achieve this level of reliability is available from the Instrumentation, Systems and Automation Society (ISA) (17) and CCPS (13–15). Stickles, *et al.*, discuss determining SIL requirements using fault tree analysis (18).

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