

Relief System Design For Reactive Systems – Get The Facts

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Do you suffer from the ERS design ostrich syndrome?

Most companies are well equipped to perform relief system design for single-phase flow and non-reactive systems. Existing standards and recommended engineering practices developed by industry associations such as ASME^a, NFPA^b, API^c, and the Center for Chemical Process Safety guideline books provide enough guidance to allow a competent engineer with proper training to perform such calculations with a high degree of confidence.

Reactive systems however, present additional degrees of complexity: (1) The reactive characteristics of the material should be well understood by the ERS designer, including the potential for reacting with itself, decomposing, rearranging, or reacting with contaminants such as water, air, rust, and other materials that could be present in the system; (2) all reactions that could occur should be identified and the kinetics of these reactions should be determined either by experiment or through trusted literature sources; (3) the characteristics of the vessel contents must be known so that two-phase flow methods may be utilized as deemed appropriate.

Common scenarios considered for reactive systems include process-induced and fire-induced runaways. Process-induced runaways include scenarios such as loss of agitation, catalyst mischarge, reactant mischarge, loss of cooling, reactant accumulation caused by low temperature or insufficient catalyst, excess steam/heat, addition of incompatible materials, etc.

In short, analyses for reactive chemicals emergency relief systems (ERS) design require skill, specialization, extensive training, and the proper tools. As an analogy, would you entrust a family doctor to perform open-heart surgery on you? Of course not; but some operating companies and engineering contractors are using general practitioners to perform the work that actually requires a specialist.

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^a ASME: American Society of Mechanical Engineers

^b NFPA: National Fire Protection Association

^c API: American Petroleum Institute

Many operating companies today are outsourcing their ERS design to outside contractors. Operating companies and engineering contractors that do not possess the resident expertise required to deal with such systems should seek expert help. They should consider the possibility for runaway reactions for all reactive chemicals. To ignore the potential for runaway reaction, or to simply state that a runaway reaction is not credible is irresponsible, extremely risky, and could be very hazardous. If an analysis is done that shows that a runaway reaction is not credible, the reasons for this conclusion must be well documented. The designer however, should keep in mind that while a material may not normally be reactive at normal operating conditions, it might be at relief conditions depending on the set point of the relief device, the nature of the vessel contents (foamy vs. non-foamy), contamination, composition, and flow regime.

If you, or your contractors are discounting such scenarios without proper justification, you are exposing your facility to extreme risk. Either you, or your contractor is 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 (RAGAGEP) require the pressure relief system to be sized for the worst credible overpressurization scenario^{1, 2, 3}. In order to identify the worst-case scenario, the design engineer should first identify all possible overpressurization scenarios. A good resource for identifying these scenarios is the most recent HAZOP study. A well executed HAZOP study will have identified the equipment, administrative and human failures that can lead to overpressurization of the vessel, and potential loss of containment. The design engineer should however, ensure that all potential overpressurization scenarios were identified by the HAZOP team. This requires a review of (1) 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 (i.e. rust, water, oxygen, chemical impurities, etc.); (2) information about the chemistry of the process including all possible reactions that can take place between the identified chemicals, including self reactions, polymerizations, decompositions, and rearrangements and the effects of contaminants on these reactions; (3) the P&IDs to identify the instruments, piping and equipment associated with the vessel; and (4) the drawings for the vessel and associated equipment to determine volumes, surface areas, materials of construction, instrument ranges and alarm/interlock set-points, etc.. Armed with this information and the HAZOP study, the design engineer should determine what can go wrong. This requires intense brainstorming. API 521 is a good reference for starting the brainstorming process. It lists common causes of overpressure and design considerations⁴. SGM is also an established scenario identification technique used by some companies. Be cautious however; of all of the codes, standards, and recommended practices, only the DIERS methodology is widely recognized for sizing relief devices for reactive service.

Careful scrutiny of the information available should be performed to determine if there is a potential for runaway reaction. If the vessel contains reactive chemicals, there is a high probability that a runaway reaction, in particular if fire induced, will be the worst case scenario. Be particularly cautious of any material that has an NFPA instability rating of 1 or higher⁵, or which is identified as reactive, or has reactive properties listed on the MSDS. Think negative; think of every thing that can go wrong.

Emergency relief systems design for reactive systems is about chemistry. Reactive systems are not forgiving. Exothermic reactions generate heat, which causes the temperature in the vessel to rise. Typically, a reaction rate doubles every ten degrees Celsius. If there is insufficient cooling, these phenomena lead to an exponential increase in temperature and pressure, an uncontrollable runaway reaction.

The importance of knowing the proper reaction kinetics cannot be overemphasized. In many cases, it 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. Further, it can either 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. This can make an otherwise non-credible runaway reaction become credible.

The design process for reactive systems is complex because of the reaction dynamics that take place. Reaction rates are temperature and concentration dependent. As a result, one is rarely able to design a proper relief system involving runaway reaction without dynamic simulation tools and/or adiabatic calorimetry testing.

How do I screen for reactivity?

Numerous theoretical, computational and experimental reactivity screening tools can easily be used to screen for reactivity^{6,7}.

Theoretical and computational screening checks typically include but are not limited to: Material Safety Data Sheets (MSDS); supplier recommended storage and handling practices, physical property and hazard data; chemical incompatibility matrices; literature and web reactivity data sources such as Bretherick's⁸ and NFPA hazards ratings; incident data from facilities handling similar materials; chemical structure and molecular bonds; formation energies, heats of reactions (polymerization, decomposition, solution); computed adiabatic reaction temperature (CART); and oxygen balance. A variety of software tools exist to aid in reactivity screening such as the NOAA web-based chemical interaction matrix utility⁹, NASA's CET93¹⁰, NIST SP program¹¹, ASTM CHETAH¹², and SuperChems, etc.

Experimental screening tests often include a blasting cap test, a flame test, a gram scale heating test, a drop weight test, thermogravimetric analysis (TGA), differential thermal analysis (DTA), the reactive systems screening tools (RSST), and differential scanning calorimetry (DSC).

What practices, standards, and regulations should I follow when I perform relief systems design?

It is not uncommon to find conflicts when reviewing Federal regulations and recommended practices, codes, and guidelines issued by different organizations. A few of these conflicts can be found concerning the design of pressure relief systems. When faced with conflicting methodologies or design standards and guidelines, the designer should, at a minimum, meet or exceed the Federal regulation requirements of OSHA¹³ and EPA RMP¹⁴ regulations. When there is a conflict between the guidance provided by the consensus codes, the prudent engineer will use the guidance that provides the most conservative design. The American Institute of Chemical Engineers (AIChE) Center for Chemical Process Safety (CCPS) has published extensively on relief system design^{15, 16, 17}. The AIChE Design Institute for Emergency Relief Systems¹⁸ (DIERS) and DIERS Users Group continue to publish and to fund research on important relief design issues facing operating companies.

Fire induced runaways

If a facility stores or handles large amounts of flammable material onsite, especially if they are stored or handled above their flash point, fire is a credible scenario and a fire induced runaway reaction should be considered. Relief requirements for fire induced runaway reactions are almost always larger than relief requirements for a process induced runaway. A fire causes the temperature of a reactive material to attain the onset of a runaway with little reactant consumption. This leaves more reactant to react and generate heat and pressure. The impact of the additional heating on reaction rates is exponential.

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 systems for reactive materials to reduce the impact of fire and to obtain a reasonable relief requirement.

What is the right fire flux to use for relief systems design?

The reader should recognize by now that the fire flux is an extremely important design variable when considering a reactive system. Common formulas used for calculating fire heat input into the vessel can be obtained from API (520/521/2000), NFPA-30, and OSHA 1910.106. Unfortunately, the API and NFPA-30 fire formulas do not agree on the value of the fire flux. NFPA-30 is more conservative than API-520/521 [up to wetted area of 2800 ft²]. The OSHA standard uses the NFPA-30 formulas.

In addition, OSHA issued three interpretation letters on this subject¹⁹. For above ground storage vessels, if your material is a PSM regulated material, you should use the OSHA formulas for fire flux and insulation credit. In this case, the insulation credit provided by OSHA is 0.3 and does not depend on insulation thickness. In 1997, experiments conducted by NFPA showed that the heating rate estimated by API is underestimated by a factor of three for hexane and overestimated by a factor of 1.8 for ethanol²⁰.

Over the past four decades fire researchers have measured (in small and large scale) experimentally the flame emissive power / fire flux of many hydrocarbon fuels from pool fire and flame jets as well as burning rates and flame length / height correlations. For many fuels, it is now possible to get 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 that are 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 wetted surface area when estimating heat input into the vessel. Existing guidelines from API and NFPA-30 ignore the impact of two-phase flow on wetted area selection and can lead to non-conservative designs. Assuming a constant heat flux input, a vessel that is 30 % full, for example, will result in a higher reaction rate than a vessel that is 90 % full. This effect has to be established using advanced simulation techniques such as those embodied in SuperChems Expert and SuperChems for DIERS.

For vertical vessels, API considers only the first 25 feet of elevation above grade as being exposed to the flame from a pool fire. NFPA 30 and OSHA 1910.106 require that the first 30 feet be considered as exposed to the flame. At a minimum, the first 30 feet needs to be considered in order to be in compliance with Federal regulations. Pool fires however, actually produce flames that may be hundreds of feet high. Many prudent engineers assume that the entire vessel, regardless of height, will be exposed to the flame from a pool fire when determining the heat input rate from fire exposure.

Should I insulate my reactive storage tank?

Insulation is commonly used to minimize heat input to a vessel when it is exposed to a fire²². However, keep in mind that 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, consideration should be given to how the vessel contents can be drained, cooled, inhibited, or utilized in the process before the material starts to runaway. 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 need to be used; will the investigating agencies (Fire Marshal, OSHA, Chemical Safety Board) permit entry into the area? Because of these unknowns, deluge systems should also be considered.

If you must insulate vessels containing reactive chemicals, a clear understanding of the runaway reactions characteristics should be obtained from adiabatic calorimetry data. Use proven dynamic simulation computer codes such as SuperChems Expert or SuperChems for DIERS to: (1) establish the required relief capacity, (2) establish the time to maximum rate, and (3) and establish the required response time for corrective actions for the proposed insulation thickness.

Should I size for two-phase venting?

For polymer systems, systems known to be sensitive to peroxidation, systems in dirty service, known foamers, etc. you should assume foamy behavior. For many gassy/hybrid systems, all gas/vapor flow should be considered because active ingredients may be concentrated during all gas/vapor venting which leads to a more dangerous situation. When faced with uncertainties of design basis caused by the choice of complex methods or limited data, the designer should select the conservative basis. The designer should also weigh the advantage of expending resources to reduce uncertainties and complexities to an acceptable level vs. the cost advantage of a more simple, but conservative design basis.

What about high-viscosity two-phase venting?

High viscosity two-phase venting occurs in many industrial scale reactors handling polymer systems²⁴. For example, a runaway reaction in a monomer tank produces viscous polymers that can lead to high viscosity two-phase flow that must be vented through the reactor's emergency relief system.

Many polymerization reactors are equipped with relief devices with discharge lines that are 50 to 100 feet long and in some cases longer. Discharge lines are typically connected to a vent containment header and/or a flare header. A large majority of relief device installations that exist today were designed using best industry practices such as API-520. A recent study of 14, 873 pressure relief devices showed that 33% of the relief devices

had excessive inlet pressure drop and 49% had excessive outlet pressure drop²⁵. These studies were based on work done by companies to comply with the OSHA PSM rule, which requires that the relief device design and design basis be verified as being appropriately evaluated and documented.

What is alarming is that these published numbers refer to relief devices that were incorrectly sized for all liquid or all vapor flow for low viscosity systems. The design of a relief valve for a two-phase discharge introduces many complications. One now has to deal with fluid systems that have the density of a liquid and the compressibility of a gas. Several attempts have been made to bring best industry practices to a point where simple techniques can be used by ERS design engineers to produce a best estimate of a safe design.

Until recently, a widely accepted method on designing a relief system for high viscosity two-phase flow did not exist. To overcome this problem, the DIERS Users Group sponsored three research projects focused on obtaining such a methodology. SuperChems for DIERS was recently released by the AIChE/DIERS Users Group and includes consensus-based techniques.

To point out a few problems that even the novice designer will quickly recognize:

- 1. How does one calculate a two-phase viscosity to use for the estimation of two-phase pressure drop in the inlet line and the outlet line?*
- 2. Is there a two-phase flow Reynolds's number? How do I compute it?*
- 3. I know that the choke point for a two-phase mixture is influenced by quality and viscosity. How do I estimate the vapor quality and associated pressure drop at the right location?*
- 4. Does a high-viscosity two-phase mixture separate in the relief valve or in the discharge pipe?*
- 5. How sensitive is the final design to small changes in inlet vapor quality?*

Item 1 is at the heart of the problem of two-phase high viscosity flow. There have been several publications over the past thirty years that suggest that a “volume averaged” two-phase viscosity should be used. Variations on this theme were also published assigning different weighting factors to the vapor or liquid portion of the flow.

A key finding of the DIERS research program on high viscosity two-phase flow is that a high viscosity two-phase discharge will separate in the discharge line. This is important since slip flow will lead to 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 discussed above 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 set pressure. The introduction of slip in the inlet line for non-viscous systems will 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) flow and viscosity model. A two-phase mixture entering the nozzle of a relief valve strikes the disc surface and changes direction by 90 degrees. At the disc surface, the fluid 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 less than two-phase flow with low viscosity 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 is less than four inches.

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

Should I look at other overpressurization safeguards when I design relief systems?

Absolutely. A relief system offers only one layer of protection against a runaway reaction, which usually has the potential to cause severe consequences including the potential for loss of life, severe personal injury, loss of capital equipment, and loss of production. 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 for enhancing the reliability of the pressure relief devices. 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 all²⁶. When the consequences of failure of the relief devices are high, this level of reliability is not acceptable. Besides 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 off 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 of this inlet line.

Reactive systems require at a minimum, temperature and pressure monitors that readout in the control room and which have high and high-high alarms. These instruments will

add two layers of protection if they have sufficient reliability. Many companies consider a high alarm and 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 usually severe, it is usually necessary to provide redundant temperature and pressure (Safety Integrity Level 2 or 3) instrumentation in order to obtain the required reliability for these safeguards. For example, when three temperature sensors of different designs are installed to avoid the common mode failure, the computer control system 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 necessary. 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 take immediate corrective actions. The interlocks are typically designed to slow or stop the runaway reaction by either: 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.

What if it is not practical to size a relief system for a specific scenario involving energetic chemistry?

If the required relief device for a runaway reaction is too large to be practical, provide additional layers of protection that will prevent the runaway reaction from occurring through Layer Of Protection Analysis [LOPA]. If the required relief device for a runaway reaction is so large that it would be impractical to install such a relief device on the vessel, the design engineer can not just declare that it is not practical to install a relief device for the worse case scenario and size the relief device for the second to the worse case scenario. The design engineer should also provide engineering controls that will reduce the likelihood of the runaway reaction to such a low value that that scenario can be judged to be non-credible, and then proceed to design for the new worst case scenario.

To achieve this, additional layers of protection will need to be added to the vessel that will provide corrective actions that will prevent the runaway reaction from occurring, or mitigating the runaway reaction after it starts. The number of layers of protection required will need to 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 2211²⁷ (in progress), and CCPS^{28, 29, 30} provide guidance on performing this risk assessment. Also see the paper on “How much Safety is Enough” by Melhem and Stickles³¹. The object 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 will need to be provided to ensure the reliability of the instrumentation. Guidance on the system requirements needed to achieve this level of reliability can be found in ISA³² and CCPS publications³⁸. Stickles et al. have also published guidance on determining SIL levels requirements using Fault Tree analysis³³.

How does one obtain calorimetry data for relief 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^d), the Automated Pressure Tracking Adiabatic Calorimeter (APTAC^e) and EuroARC are used by many companies and ERS consultants in the US and internationally to collect the thermo kinetic data under near adiabatic conditions that are required to size the relief devices for reactive systems. The Reaction Calorimeter (RC1^f) is also used (with caution) to obtain heats of reaction data and to simulate actual reaction processes in a 1 liter scale.

Other useful instruments that can also be used include vent sizing instruments such as the Advanced Reactive Systems Screening Tool (ARSST^g), the Vent Sizing Package (VSP2^h), and PHI-TEC.

Thermal inertia: friend or foe?

Although this is highly debated by the various calorimeter vendors, thermal inertia is more of a friend than foe. Thermal inertia is a measure of the thermal capacity of the test cell and the contained sample compared to the thermal capacity of the sample. 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 one degree. A very large plant-scale vessel will have a thermal inertia close to 1, i.e. the vessel thermal capacity is small compared to the material thermal capacity. This is especially true during a runaway reaction when the temperature of the reaction mass is rising very rapidly and the heat transfer rate to the vessel is insufficient to allow the vessel temperature to rise at the same rate.

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

^d The ARC is a registered trademark of TIAX, LLC.

^e The APTAC is a trademark of TIAX, LLC.

^f The RC1 is a trademark of Mettler-Toledo

^g The RSST is a trademark of Fauske and Associates, Inc.

^h The VSP is a trademark of Fauske and Associates, Inc.

If calorimeters with high thermal inertia are utilized, ensure that the reaction selectivity is not changing with thermal inertia. Run duplicate experiments at different thermal inertia. 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 plant vessel thermal inertia value.

What tools are available for performing relief design for reactive systems?

Check out SuperChems for DIERS, a subset of SuperChems Expert marketed by the American Institute of Chemical Engineers (AIChE), if you are interested in performing ERS design for reactive systems and you know the reaction stoichiometry and kinetic data. You can also upgrade to SuperChems Expert if such data needs to be reduced from experimental measurements and the stoichiometry needs to be determined as well. In addition, SuperChems Expert offers the ability to design effluent handling systems and process headers. Details on SuperChems for DIERS and SuperChems Expert can be found on www.iomosaic.com

How can we help?

We specialize in chemical process safety. We have the experience and the necessary tools to find practical solutions to the management of reactivity hazards you may be facing. We offer a broad range of chemical process safety consulting services including: reactivity testing services, emergency relief systems design, software solutions, and risk management.

Join our Roundtable for Managing Chemical Reactivity. This group of selected industry and consulting experts meets twice a year in conjunction with the U.S. DIERS Users Group Meeting to share and exchange knowledge. Members can seek input and experience based advice from other group members on reactivity issues. This group is sponsored by ioMosaic Corporation. If you are interested in joining our Roundtable for Managing Chemical Reactivity, please contact Georges A. Melhem @ 603.893.7009 ext. 101; e-mail melhem@iomosaic.com

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Mr. Howell performed numerous root cause incident investigations throughout his career using many different methodologies and team organizations. His chemical, mechanical and engineering background, along with his creative abilities, have allowed him to successfully resolve each of these incidents.

He has performed, and supervised the performance, of all of the elements contained in OSHA's Process Safety Management regulation 29 CFR 1910.119, including compliance auditing, for numerous processes and clients.

He has prepared, or supervised the preparation of numerous policy, procedure, methodology, and protocol books, handbooks and documents related to process safety, hazardous materials and accident investigation. Refer to <http://www.markfive.com> for more information.

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