Common Pitfalls Designing Emergency Pressure Relief Venting Systems for Runaway Chemical Reactions

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An emergency pressure relief system (EPRS) is the most frequently employed Basis of Safety or layer of protection option for overpressure safeguarding in the chemical, pharmaceutical and allied industries. It can provide protection to reactors, storage tanks, columns, boilers, dryers and other processing equipment. When designed and operated properly such a system can be both cost-effective and reliable. Correct specification, operation, maintenance and inspection of the EPRS is critical for the safety of staff and the environment. However, we continue to see incidents that put some focus on the common failures along the lifecycle of the system. In this paper we analyze some of the most common pitfalls in the design of an EPRS and how to overcome them. The paper is based on real cases collected along the years by DEKRA Process Safety consultants.

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How It Should Be Done

The state-of-the-art design methods for relief systems are based upon the work of DIERS (Design Institute for Emergency Relief Systems) and subsequent supporting research¹. The principal steps in a procedure for the design of an emergency relief system follow an established flow chart as shown on this page.

Scenario Identification

An emergency relief system must be designed for one specific scenario – that which requires the largest relief capacity among all of the potential relief scenarios. There are no "one size fits all" shortcuts possible. Therefore, identification of the scenarios should be the first step in any EPRS design. Over the years, we have observed a number of deficiencies in this area: either there is no scenario identification whatsoever, or the identification missed some significant scenario.





¹ Emergency Relief System Design Using DIERS Technology. Design Institute for Emergency Relief Systems, 1992.

In some cases, we find that the relief device (disc or valve) is provided by the supplier of the vessel being protected, without any consideration for the processes carried out in it. Quite often the relief device has been dimensioned for a fire engulfment case, considering one specific fluid inside the vessel. One question often not asked is whether the fluid is thermally stable under the conditions of fire engulfment. Of course, this fluid may not be what the vessel owner intents to put in there, so the relief device may be insufficient. Over time the use of equipment is often changed, many of these changes result in the EPRS being inadequate for the new situation.

On the other hand, especially in the case of chemical reactors, it is essential to take into account the reaction being performed. A runaway chemical reaction can have a very significant thermal energy release, increasing the temperature of the reaction mass beyond cooling capacity and therefore causing overpressure. Additionally, as the temperature increases, either one of the reactants or the final product can decompose, typically releasing a gas that will contribute to overpressure. Depending on the reaction conditions the flow that needs to be released can be:

- A gas (generated by the intended reaction and/or by a secondary) thermal decomposition).
- A vapor (from the solvent or a reactant, as the temperature) increases).
- A liquid (typically part of the solvent), carried over by vapors or gases, forming foams and two-phase flows. This last case is the most common for runaway reactions and decompositions.

Other considerations should include the thermal stability of the material:

- Can the pure material decompose under storage conditions?
- ► Is it credible that the wrong material unloaded into a tank may cause a chemical reaction or polymerization to occur?

The runaway reaction incident at T2 Laboratories on December 19th, 2007 provides an excellent example where a relief device (a rupture disc) did exist, opened when the set pressure was reached and yet, it failed to relieve the pressure because it had been improperly dimensioned for the abnormal conditions encountered during the process failure, injured thirty-two and caused significant loss of property, including the total destruction of the plant. The excellent report from the U.S. Chemical Safety Board² provides more details on this case.

It is generally the case that runaway reactions or thermal decompositions require the largest venting areas (even larger than fire engulfment, traditionally the default dimensioning case). In such cases the use of relief valves may not be possible and one needs to apply rupture disks and catch systems to assure adequate venting capacity.

Venting off materials through a relief valve or rupture disk may not even be enough, as it is merely displacing the result of the release from inside a vessel to the outside world. Especially for toxic substances this may not reduce the risk sufficiently.

Investigation Report 2008-3-I-FL. T2 Laboratories, Inc. Runaway reaction (Four Killed, 32 Injured). U.S. Chemical Safety and Hazard Investigation Board. September 2009.



In these cases, other technological solutions may be required, including modification of the process or the reaction path or the application of (instrumented) safeguards that prevent the scenario from happening in the first place.

Even for simple fire relief calculations, use of the wrong formulas can result in vastly undersized relief conditions. In one scenario, the calculations did not consider that the equipment was enclosed in a concrete vault. This greatly increased the heat input to the tank, and resulted in a severely undersized relief system due to the resulting higher reaction rate. In another, credit was taken for adequate drainage and fire protection where neither existed. This again resulted in an undersized relief system. In relief scenarios associated with runaway reactions or thermal decompositions it is critical to use sound data relating to the precise conditions of the failure scenario under consideration, data which would rarely be available in the literature. Quite often, a number of laboratory tests have to be conducted in order to obtain the relevant kinetic and thermodynamic and property data. Obtaining all the data required might be costly. However, using the wrong data (for instance, for another similar reaction) can lead to a wrong sizing and is, in fact, equivalent to not having identified the scenario.

In any case, it is very clear that a relief device (in fact, the entire EPRS) is a safety critical element. Therefore, it must be designed taking into consideration the risk tolerability criteria of the owner. The only way to accomplish this is by performing a process hazard analysis and obtaining an exhaustive list of potential overpressure scenarios, their relief conditions and the risk associated. Missing runaway reaction scenarios or improper risk assessment is very typical when the plant was designed and built by an engineering company. Quite often, they refer to general standards such as API 520 and 521³ or ISO 4126, or even their own internal standards and criteria, and very rarely do those include the consideration of runaway chemical reactions or thermal decompositions. Also, quite often, the information that the owner has made available about chemical reactions is scarce or nonexistent. A modest, constant, heat input from a fire can substantially increase the kinetics of the reaction, and consequently result in undersizing of the vent. If only the reaction energy is considered, you may undersize the vent.

Calculation of **Vent Area**

Once the scenarios have been identified and characterized, the vent area required needs to be calculated. The main mistakes that we have found in this area are:

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- The calculation is insufficiently supported by chemical reaction data to quantify the kinetics and vapor pressure profile
- Scenarios with widely different flowrates are safeguarded by the same relief device.
- ► The calculated conditions of the scenario are unrealistic.

Multi-purpose reactors can be particularly challenging due to the wide range of products made in such vessels. An undersized relief system was discovered because it was assumed that the reaction with the highest reaction energy would be the worst case. However, the reaction rate was limited by mass transfer limitations from the gas to the liquid phase. The true worst case was a reaction with lower reaction energy, but without mass transfer limitations.



³ Standard 520. Sizing, Selection, and Installation of Pressure-Relieving Devices.

Some **Examples?**

It is frequently the case that the diverse scenarios identified have a wide range of required flowrates (sometimes spanning orders of magnitude). If this system is safeguarded with only one safety valve, trouble may be in store. When one of the smaller scenarios actually happens, the valve will open. Since its capacity is very large compared with that required in this case (as it was designed for the large scenario), it will very rapidly relieve some fluids, and close again as the pressure has dropped. However, the scenario is not over yet, so the pressure will build up again, causing the opening and immediate closing of the valve. Depending upon the magnitude of the oversizing, the relief valve may cycle, chatter, or flutter. Whilst the consequences of all these behaviors require examination, fast opening/closing (chattering) can cause the relief valve to stick open or closed, and in the worst case shatter the valve body. This phenomenon is called "chattering". Of course, if the system is safeguarded by a rupture disc chattering is not an issue. The following chart on the next page schematizes the chattering cycle.

An alternative approach is twin relief devices with staged set pressures, (perhaps a smaller relief valve with a lower set pressure for the 'minor' cases and a parallel bursting disc for the 'credible worst case scenario' with a higher rupture pressure). However, often there is insufficient margin between the normal operating pressure and the vessel design pressure to accommodate this approach, along with the other aspects such as high pressure alarms and trips which should operate before relief set pressures are reached.

Process designers frequently guilty of underestimating the size of margin needed for each of these protection layers to operate independently.





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Upstream and **Downstream Systems: Disposal**

All too often we observe the belief that once the gas, vapor or liquid is out of the relief device, nothing else matters. On the contrary, a bad design of pipework upstream or downstream of the relief device, or a careless disposal can render useless the best designed relief device.

The most common mistake is to connect the relief device to a convoluted piping system, either upstream, downstream, or both. We need to remember that pressure relief valves and rupture discs operate under differential pressure between upstream and downstream sides. If the opening of a relief device causes pressure build up in the collectors downstream, this may prevent other devices from opening correctly in scenarios affecting adjacent vessels.

Even if the relief device opens, the head losses in the piping can be so large that the pressure differential between the protected vessel and the final disposal point do not allow the flow rate required. Or, in other words, the pressure differential required is larger than the allowable pressure in the vessel protected, thus rendering the system ineffective.

If excessive pressure buildup downstream of a safety valve will nominally still allow the required flowrate, it can cause chattering, resultant decreased capacity and fast destruction of the valve. In this case chattering is caused by repeated cycles a shown in the following chart. The allowable limits for backpressure on a relief valve will depend upon the valve type chosen, typically conventional or balanced bellows, and rarely pilot operated.

A similar effect will be experienced due to excessive pressure drop in the inlet line.







Connecting several vessels to a common collection system is always tricky, as it can lead to interesting effects. Compatibility of pressure and composition should be checked in all cases. It is usually a bad idea to connect relief devices with very different set pressures to a common collector. If the high-pressure device opens, it can create sufficient overpressure in the collector to prevent opening of the low-pressure relief devices. Even worse, if the low-pressure devices are rupture discs, they could open backwards, thus pressurizing the low-pressure section of plant with possibly reactive materials! Consider, for instance, the following system:

R-1001 R-1002

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Disposal

The main characteristics of the two reactors are as follows:

| Characteristic | R-1001 | R-1002 |
|------------------------------|---|-------------------------------|
| Design pressure | 12 bar | 2 bar |
| Normal operating pressure | 10 bar | 1 bar |
| Design temperature | 200 °C | 50 °C |
| Normal operating temperature | 150 °C | Ambient |
| Relief system | Pressure relief valve, set at 12 bar | Rupture disc, set at 2 bar |

There are three valid solutions to this case:

- (Preferred). Collect and dispose of high and low-pressure systems separately.
- Collect both systems into an intermediate catch tank sufficiently large and well vented. The size and venting of such a vessel must be designed so that if the safety valve in R-1001 opens, the pressure buildup in the catch tank is still small enough to allow normal operation of the rupture disc of R-1002. This type of solution usually leads to enormous catch tanks and requires an extremely accurate analysis of relieving scenarios in both vessels, to guarantee the correct sizing of the catch tank.



Conduct careful sizing of the overall vent system, balancing flows and pressure profiles, and using rupture discs in series, with characteristics chosen for the downstream disc to protect the upstream one. Such a solution requires specialist analysis and important safeguarding features.

Funny things can also happen when incompatible chemicals are collected in the piping of an EPRS, if two relief devices open simultaneously. Normally the triggering of a relief device is a rare event, and the simultaneous triggering of two devices should be even rarer. However, if the vessels they safeguard are sufficiently close or share some utilities there might be common cause failures. And while simultaneous venting may be rare, sequential venting of one vessel after another can occur more frequently.



Some examples are:

- ► A fire engulfs both vessels.
- A failure in cooling water causes a runaway reaction in one reactor and the loss of cooling capacity in the condenser of a nearby distillation column.
- ► A blackout at the plant causes failure of all the aerocondensers.
- A failure of cooling to a plant containing many identical reactors
- Reactor mischarge owing to a formulation error an incident involving catalyst overcharging by a factor of 10 (decimal point error) resulted in successive rupture disc venting of ten polymerization reactors

Another case of incompatibility was once found where a seemingly harmless vent on one vessel could trigger a runaway reaction in the next next owing to incompatible chemicals.

Needless to say, plants with multipurpose reactors, where many different processes are run simultaneously, are especially prone to this type of problem. In some cases, changeout of relief devices is necessary based on the reaction being carried out in a multipurpose reactor.

Some mistakes can also happen in the disposal of fluids vented. It is usually not a good idea to vent directly to the atmosphere hazardous (flammable, toxic, corrosive, environmentally damaging, etc). Therefore, provisions must be taken to dispose of these fluids appropriately.



First of all, liquids need to be separated from the gases in the vent stream, and each each independently treated. This is usually achieved with a properly dimensioned knock out drum. Droplets are suspended in the gas due to the high speed of flow. In the knock out drum speed decreases, so that droplets are no longer suspended, they fall, and can be collected. When liquid is expected in the release, the piping design should account for the additional pressure drop and should be oriented to self drain, without pockets in low points. The relief piping and its supports must also be designed to be sufficiently robust to withstand the very high thrust and reaction forces associated with relief vent flows, frequently at sonic velocity. Accumulation of liquids in these places can lead to head losses as a best case scenario. As worst-case scenarios, one can think of:

- Pipe rupture, typically at vent, when a relief vent opens because the accumulated slug of liquid would be propelled at high velocity such an incident in a UK oil refinery resulted in release of hydrocarbon and a secondary vapor cloud explosion devastating the site
- Exothermal reactions or thermal decompositions, leading to damage to piping and uncontrolled release of hazardous materials.
- Polymerization or freezing of the liquid and the subsequent plugging of the pipe, rendering it unavailable for further use. Notice that this will be, in general, a hidden failure, that may go undetected for a long time...until some overpressure in a vessel cannot be relieved because the venting pipe is blocked downstream.

We can safely dispose of flammable gases and vapors in a flare, if such a utility exists in the facility. If not, and assuming that the gases are only flammable and the environmental regulations permits it, they could be vented at sufficient height so that the flammable atmosphere does not reach ignition sources: roads, places where people may be present, electrical or mechanical equipment not specifically designed to operate in flammable atmospheres.

opens because ed at high velocity elease of hydrocarastating the site s, leading to damdous materials. subsequent plugther use. Notice that y go undetected for cannot be relieved n. When the gases or vapors are toxic or corrosive, they need to be treated in a flare or scrubber or, regulations permitting, be vented at sufficient height to be dispersed without causing harm. At present authorities or regulatory bodies are often requesting dispersion calculations to prove that concentrations at ground level will be harmless.

In the case of runaway reactions, a good solution is a quench tank. This passive scrubbing tank is designed to break the foaming 2-phase flow allowing the liquid to be retained, condense the vapor proportion of the gas phase, and possibly also scrub gases. Such a quench tank design for a plant handling pyrophoric chemicals conducted by DEKRA in the UK, won the 2001 IChemE Safety Award.

These disposal requirements often induce mistakes that, once again, limit the effectiveness of the EPRS. Reliability of an EPRS should always be considered as its fundamental design principle. If the EPRS fails, there will be an unallowable overpressure somewhere, causing catastrophic failure of vessels or other equipment, releasing hazardous materials in an uncontrolled manner, and creating blast waves. The relief devices (safety valves and rupture discs) have, themselves, a very simple design, in order to maximize reliability.

Thus, the rest of the EPRS system (piping, valves, disposal systems) should have a similarly simple design. If a scrubber or a flare is the disposal systems of choice, their reliability must be guaranteed at the required level. And this includes, of course, periodic verification. Manual valve at any point in the EPRS route in any place of an EPRS, if they cannot be avoided altogether, are always to be closely monitored, as they can become a reliability bottleneck for the entire system. A system for locking manual valves in their safe positions is certainly a requirement in these cases.







Documentation

Poor documentation of an EPRS does not normally prevent its correct operation ... at least if the plant does not suffer any change. When one wants to introduce any change (a new reactant, catalyst or solvent, a different operating temperature, a new order of additions, a higher vessel loading, or an entirely new process...) the problem arises as nobody will be able to tell whether:

- The changes give rise to new relief scenarios.
- The existing relief scenarios are still valid.
- ► The relief conditions are still valid.
- The risk associated to the existing scenarios has increased.
- ▶ If the system has sufficient capacity and reliability to safeguard any new scenarios, and any changes in the existing scenarios.

If the process safety culture of the owner of the plant is sufficiently high a poor documentation will lead to a re-design of the system. And For instance, Hedlund et al.⁴ report a case where a rupture disc was in some jurisdictions, the regulator will not accept poor documentation installed upside down because of a misreading of the drawings. and will insist on compliance to good standards to allow continued Nobody checked the installation. As a consequence, a 90 m³ tank weighting 4 tons lifted off like a rocket, rose to about 30 m and landed plant operation.



Relief valve with insufficient support and manual valve

Installation

We have all heard many stories about mistakes in the erection of industrial plants, and how construction must be checked carefully before startup. EPRSs have a couple of characteristics, worth considering in this context:

- Usually they are the ultimate layer of protection. If they fail, we can expect a catastrophic failure.
- ► They fail on demand. Therefore, we could only be sure that they are in a proper condition by testing. However, pressure relief valves are difficult to test in situ, and rupture discs cannot be tested at all.

Therefore, a pre-startup safety review (PSSR) program is an absolute must when the project involves an EPRS. When failing to do so you can compromise seriously the safety of the plant.

Hedlund, FH et al., Large Steel Tank Fails and Rockets to Height of 30 meters – Rupture Disc Installed Incorrectly, Safety and Health at Work

Relief valve with pressure gauge

Bended relief line caused by an explosion and insufficient support



on a van. Fortunately, there were no injuries. We have also seen things like blind flanges left at the inlet of pressure relief valves after a pressure test of the vessel they were intended to protect. In another case plastic caps installed by the overhaul company to protect the valves from contamination were not removed by the installation contractor.

In other cases the piping to and from the EPRS causes problem, the mechanical forces during venting are significant, and may result in movements of the pipework, bending and subsequent blocking of the vent. In one such case, the blocking of a vent line resulted in rupture of a reactor, debris ejected 50 m, and flames punching a hole in the building roof and rising to a height of 30 m. For 2-phase flow from runaway reactions along large bore vent lines, the reaction forces can be huge, and we have seen cases where the strength of the building structure was insufficient to allow the vent line to be correctly anchored. And other cases where rupture of the vent line due to poor anchoring caused a secondary and far more severe incident. This shows the importance of PSSR for EVERY startup, not just when the equipment is new.

Maintenance and Inspection

As any other layer of protection that operates on demand, the status of an EPRS can only be checked by:

- Demanding it to work.
- ► Testing it.

Relying on the system to work without any inspection is not a good idea, as equipment tends to deteriorate as times goes by. Especially if the ambient is aggressive.

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We have seen cases where a small leak in a rupture disk or safety valve has resulted in condensed liquid sitting atop the relief device, resulting in an increased opening/burst pressure. In the case of a rupture disk and safety valve in series, a small leak in the disc can result in pressure trapped between the relief valve and disk. This again will result in a higher burst pressure than intended. All installations involving series devices will require venting of the interspace and detection of pressure build-up. There is a potential advantage in installing two parallel relief devices, allowing one to be serviced while the other is in service. This can also avoid have to empty and clean a hazardous material tank before removing the relief device. However, the changeover valving must be mechanically linked to prevent simultaneous closure of both routes.

The only way to maintain reliability of the system is, therefore, to inspect periodically its components. The obvious question is then, what should be the frequency of inspection? Some years ago, corporations developed their own standards. The contemporary answer to the question above is: it depends on the risk that the system is safeguarding; the higher the risk, the more frequent inspection is required. There is another parameter taken into consideration, as the intrinsic reliability of different pieces of equipment may be different or, in other words, some equipment tends to be rendered unreliable or ineffective depending upon the conditions of use (e.g. polymer solids blocking relief valve inlets). Risk-based inspection and riskbased maintenance, as supported by recommended practices such as ANSI/API RP 5808 and API RP 5819, give very detailed procedures to determine maintenance and inspection frequencies. But maintenance and inspection frequencies should be reviewed according to site experience gained during the inspection.



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Management of **Change**

As we all know, poor management of change is the origin of all sorts of troubles in process plants. It is clear that by introducing changes in the process, one can generate any of the mistakes described above, even if the EPRS was perfectly designed to begin with. Therefore, any management of change process should include the review of the entire EPRS, not only the valves or discs as often happens. For instance, after a capacity expansion in a continuous process manufacturing plant, we discovered that the flare was insufficient to cope with the largest release scenario. We had, therefore, to design an alternative safeguard for this specific scenario: a High Integrity Pressure Protection System (HIPPS).

In batch plants it is often that higher demands result in higher vessel loadings. This may render the EPRS too small as the original design was for relieving gases, while the new situation results in 2-phase flows which require much larger vent areas.

Conclusions

A well designed, operated and maintained EPRS is a cost efficient highly reliable safeguard against unallowable overpressure in process plants. However, there are a number of common mistakes that can render the system inefficient or insufficiently reliable. Being normally the last layer of protection before a catastrophic failure and release of hazardous materials and energy, special care should be taken along the entire lifecycle of the system. Also, all the auxiliary equipment (pipes, disposal systems...) should be given the same attention as the relief devices (valves, discs) themselves - the whole system is the safety critical protection measure!







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Keith Middle joined DEKRA in 1994 and has since become a Principal Process Safety Specialist in the Process Safety Consultancy. Before this, he worked for BP Chemicals in the UK and France for 16 years. He has considerable experience within the fields of polymers, specialty and fine chemicals and petrochemicals. His expertise covers process hazard identification, assessment of chemical reaction hazards and the provision of practical engineering solutions. Particular specialties include HAZOP leadership, SIL determination to IEC 61508/11, the design of emergency relief systems using DIERS techniques, and the specification of vent treatment systems. He is a Chartered Engineer and a Fellow of the Institution of Chemical Engineers.

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