

AVOID PRESSURE RELIEF VALVE PLUGGING IN GAS CONDITIONING APPLICATIONS

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ABSTRACT

Pressure relief valves (PRVs) are critical safety equipment that must reliably perform during an overpressure event. A problem that has occurred in gas handling and refining facilities is the plugging of PRVs and piping by solids or hydrates. Engineers and operators must be aware of the conditions, stream component concentrations, physical properties, reactions and other situational factors that contribute to solids formation, deposition and buildup in PRV piping. In this paper, Trimeric identifies systems and locations where the potential for solids may occur, and ideas engineers and operators may implement to avoid plugging of the PRV. The paper will discuss and include photographs of actual plugged relief systems.

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Introduction

Pressure relief valves (PRVs) are intended for use in applications for which vapors, liquids, or vapor-liquid mixtures are vented to prevent overpressure in process equipment and piping systems. PRVs are credited with a high reliability in process hazard analysis and are expected to work when needed. PRVs generally are not designed to handle vent streams that contain a significant concentration of solids or that can form solids and plug the PRV inlet and/or outlet or piping. Guidelines provided by industry references for how to avoid plugging in PRVs tend to be generic. For example, the American Petroleum Institute (API) Standard 521 "Pressure Relieving and Depressuring Systems" indicates that the formation of solids that can lead to plugging "should also be considered in the design." This paper 1) describes common process conditions that can lead to plugging of PRVs, 2) provides suggestions for process design options to mitigate or avoid PRV plugging, and 3) summarizes case studies demonstrating how PRV systems can plug and recommendations for preventing plugging.

Situations Amenable to PRV Plugging

There are a wide variety of situations that theoretically can result in PRV plugging that are covered in this section:

- Freezing
- Hydrate and/or Ice Formation
- Reaction Products
- Precipitation
- Non-Steady State Operations
- Solids Entrainment

Freezing

Cold weather is the obvious cause for freezing. Less obvious but a prime candidate for PRV plugging is a process that operates at elevated temperature so that material that would be solid at ambient temperatures remains liquid or vapor. PRV inlet pipes usually are dead legs that have a different temperature than the main process. The pipe skin temperature and process fluids can cool to below normal process temperatures over time even if the piping is insulated. Examples include aqueous systems, molten sulfur, and hydrocarbon waxes, paraffinic crudes or heavy oils.

The Joule-Thomson (JT) effect that occurs when gases expand due to the pressure drop across a PRV leads to low temperatures that can result in freezing and generation of significant solids buildup that can plug the PRV and/or outlet piping. Carbon dioxide (CO₂) can form solid dry ice when the pressure is let down, and, in fact, the conventional dry ice manufacturing process uses this approach. CO₂ at elevated pressure will form dry ice on isenthalpic expansion to atmospheric

pressure across a valve. A photo of liquid CO₂ vented from a pipeline at approximately 1200 psig is provided in Figure 1. The cloud and white material on the ground is solid dry ice. The solid material could accumulate in the PRV outlet chamber or in the outlet piping if it were a closed system instead of a local vent to atmosphere.



Figure 1. Example of Dry Ice Formation Due to Venting Liquid CO₂.

Hydrate and/or Ice Formation

Hydrocarbon systems that contain water are susceptible to hydrate formation that can result in plugging of PRVs. For example, typical associated natural gas that contains substantial concentrations of ethane and propane may have hydrate formation temperatures as high as 50 °F at modest pressures (300-500 psig). The presence of hydrogen sulfide (H₂S) increases the hydrate formation temperature. It is highly probable that dead legs on the PRV inlet line could see temperatures below 50 °F during cold ambient temperature without features designed specifically to prevent the low temperatures. JT cooling across the PRV could lead to extremely low temperatures and the possibility of hydrate formation in the PRV outlet chamber or piping. Acid gas streams with high H₂S concentration, such as in the headspace of some sour water stripper (SWS) units, are particularly susceptible to H₂S hydrate formation. Gases with H₂S partial pressure of 50 psia can form hydrates in the range of 40-50 °F.

Hydrocarbon systems that also contain water may form ice downstream of the PRV due to JT cooling. Examples include scrubbers, three-phase separators, and water-wash systems. The ice could have similar properties to hydrates but would form at lower temperatures and perhaps melt or sublime at a different rate.

When there are multiple credible relief cases, the PRV typically is sized for the relief case requiring the largest PRV orifice. The relieving conditions and fluids to be relieved may vary considerably from case-to-case, and all credible relief cases may not be modeled in as much detail as the sizing case during detailed engineering. For example, the relieving fluid in a fire case usually is at elevated temperature and would not reach low enough temperature by JT cooling downstream of the PRV to form hydrates. The same PRV could also need to protect against a blocked discharge or thermal relief case. The PRV inlet fluid for the alternate cases would be at a lower temperature than for the fire case. In fact, it would be common for the PRV inlet fluid to be at approximately ambient temperature for the alternate cases. PRV inlet piping can have a lengthy stagnant leg to provide the elevation necessary for the discharge to enter the flare header without pooling liquids. The fluid in the stagnant leg would reach ambient temperature over time, even with insulation. JT expansion across the PRV is much more likely to result in extremely low temperatures if starting from ambient temperature than from the elevated fire case temperature. The non-sizing relief cases may result in frequent opening and closing of the PRV because the full PRV capacity is excessive for the smaller relief load and may create potential for the PRV to “simmer” if the valve does not fully lift or fully reseal. The simmering behavior is more likely to allow for hydrate or ice formation in the PRV outlet chamber and outlet piping because the low flow rates are not sufficient to sweep the solid material away.

Reaction Products

The reaction of vapor phase components to form solid products is a known mechanism for plugging of PRV inlet lines. Trimeric has identified at least three refineries that have experienced plugging in PRV inlet lines in sour water stripper (SWS) service. SWS service is particularly challenging because of the presence of multiple reactive species, including ammonia (NH₃), hydrogen sulfide (H₂S), and carbon dioxide (CO₂). The photos below are from the PRV inlet line on the SWS reflux drum service in a large gulf-coast refinery (Figure 2), from a Chevron refinery (Figure 3), and from an unidentified refinery (Figure 4). The solids are thought to be either ammonium sulfide salts, ammonium carbonate [(NH₄)₂CO₃], or a combination. The solid material is created by the reaction of vapor constituents in the SWS reflux drum or other vessel headspace and deposition onto surfaces at temperatures below the decomposition temperature of the salts. Standard heat tracing for moisture freeze protection is not hot enough to prevent the formation of solid ammonium bicarbonate [NH₄HCO₃] in this part of the process (see the Practices to Avoid Plugging section for suggestions to mitigate the PRV inlet plugging). Near 175-180 °F ammonium bisulfide salt will precipitate from the vapor phase to form a solid. Decomposition or melting temperatures for ammonium compounds that may form in the SWS systems include the following:¹

- Ammonium carbonate hydrate 136 °F (58 °C)
- Ammonium bicarbonate 97-140 °F (36-60 °C)
- Ammonium carbamate 140 °F (60 °C)
- Ammonium bisulfide or ammonium hydrosulfide [NH₄SH] 244 °F (118 °C)

Elemental sulfur can form in systems that use nitrite-based liquid scavengers for H₂S removal. The elemental sulfur is insoluble in the liquid and could drop out in stagnant areas like PRV inlet piping.

¹ Lide, D.R., ed. *CRC Handbook of Chemistry and Physics*, 71st edition. CRC Press, Boca Raton, 1990.

Alternative methods of overpressure protection are required for polymerization reactors in the petrochemical industry due to the high likelihood of reaction products plugging any vent piping. Polymerization reactions are not common in gas processing applications and so are not addressed in any more detail here.

Precipitation

Aqueous solutions, such as are found in amine treaters and caustic scrubbers, are common in the gas processing industry. It is common for high concentrations of salts to accumulate in the aqueous solutions, in some cases approaching the solubility limit. Heat loss from the stagnant inlet pipe could reduce the temperature below the limit at which the salts are soluble, resulting in precipitation of solids. The salts also could drop out on hot surfaces or in vapor headspace where the bulk liquid evaporates. The process conditions during a relief event often are different from the normal operating conditions. Temperature or pressure changes could shift the conditions from soluble to insoluble. Additionally, some of the liquid could evaporate at low pressure on the downstream side of the PRV, resulting in deposition of salts from that fraction of the fluid.



Figure 2. PRV Inlet Piping on Headspace of Sour Water Stripper (large gulf coast refinery).

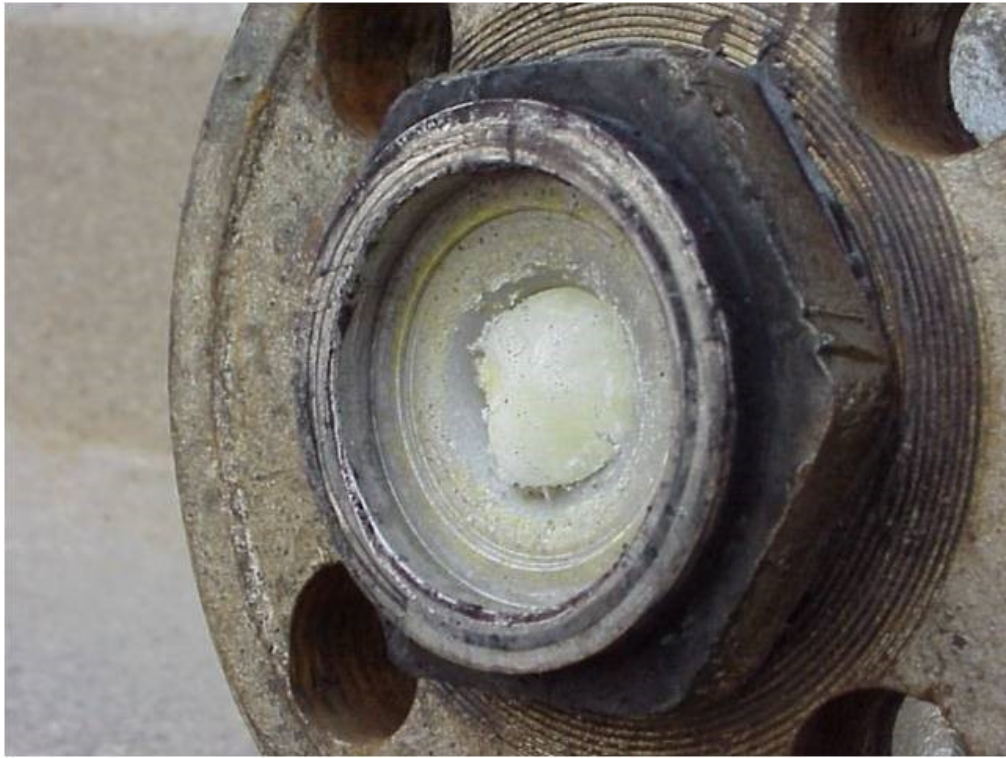


Figure 3. PRV Inlet Piping on Headspace of Sour Water Stripper (courtesy of Chevron).



Figure 4. PRV Inlet Piping on Headspace of Sour Water Stripper (unidentified refinery).

Non-Steady State Operations

The process conditions during startup and shutdown may be significantly different from the conditions in the steady-state material balance. Processes that operate at elevated temperature are particularly susceptible to plugging when started up from a cold condition. The hydrate and ice situation described above occurred when the process unit was out of service and not at the normal operating conditions.

Solids Entrainment

Solids entrained in the process fluid inadvertently could lead to plugging in PRV dead legs or even when the PRV lifts if the solids concentration is high enough. Examples of common entrained solids are sand with produced fluids, corrosion products, and construction debris.

Practices to Avoid Plugging

It is not always possible to design a process system to avoid or prevent solids from forming that can plug PRV installations, and sometimes the presence of solids is revealed through experience. Recommended practices to avoid plugging in solids prone pressure relief systems are summarized in this section.

- Heat Trace and Insulation
- Inert Gas Purge
- PRV Selections to Consider for Solids Prone Systems
- Safety Instrumented System (SIS)

Heat Trace and Insulation

The most straightforward method for avoiding precipitation of salts or the formation of hydrates or ice is to install heat tracing and insulation that is commonly used for freeze protection in process systems. There are few, if any, industry standards that provide specific guidance about how to design hydrate or freeze protection heat tracing for relief systems. API 521 suggests that heat tracing may be required for valves and discharge lines to avoid solidification (7th edition, Section 5.2.4). The previous version of API 521 noted that “No uniformly accepted method has been established for reducing the possibility of plugging” for cooling by JT expansion across a PRV (6th edition, Section 4.9.2).

Three options (or a combination of the options) may be considered for hydrate or freeze protection in relief systems:

- Heat the outlet piping so that its temperature is above the hydrate or ice formation temperature.
- Heat the inlet piping so that the discharged fluid will remain above the hydrate or ice formation temperature after JT cooling across the PRV.
- Heat the PRV itself.

Heat tracing generally is designed to maintain the temperature of a stagnant system by offsetting heat loss to the surroundings. Solid plugs of hydrate and/or ice would be unlikely to form due to kinetic limitation when the PRV is wide open with the full rated flow. In any case, standard heat tracing does not have enough energy density to heat a flowing fluid. Standard heat tracing on the PRV and outlet piping may or may not provide adequate protection against plugging if extremely low temperatures are encountered, such as the example of a PRV “simmering.” The rate of heat input from standard tracing may be insufficient to melt hydrates or ice. Designers may need to consider maintaining a higher temperature than normal so that there is enough residual heat in the PRV and piping to avoid hydrate or ice formation when the PRV first begins to relieve.

Heat tracing the stagnant inlet piping so that the relieving fluid does not drop below the hydrate or ice formation temperature due to JT cooling would be a more reliable protection for the relatively low flowrate “simmering” situation. The stagnant fluid in the inlet piping could be maintained at the set point temperature because there is normally no flow. Each time the valve relieves and closes, the heat tracing may be able to bring the stagnant fluid back to the set point temperature.

The PRV itself may be heated using standard heat trace tape or steam tubing, by a flexible or bolt-on jacket, a blanket, or with a heated enclosure. In general, the PRV probably should be heated when the adjacent piping is heated. Heating the PRV sufficiently can help the valve function properly to open and reseal. Additionally, heating a conventional PRV can prevent condensation from freezing due to low ambient temperatures around the spring in the bonnet which is exposed to the discharge-side process fluids.

An example electrical heat tracing design for a pilot-operated PRV is provided in Figure 5. It is important that the sensing lines be appropriately heat traced and insulated.

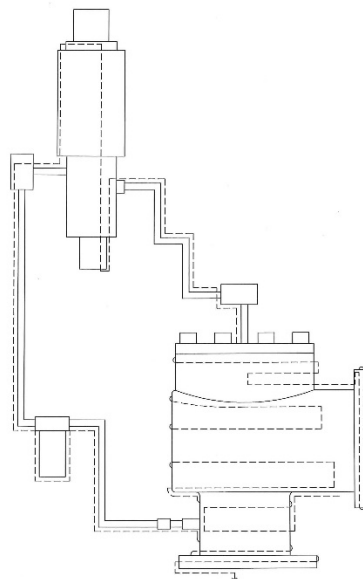


Figure 5. Example PRV Heat Tracing Design (courtesy of Thermon).

The example cases shown in Figure 2 through Figure 4 were systems that used high-temperature steam tracing because the potential for solids formation was known. Unfortunately, the heat tracing was not operating as designed to maintain the temperature above the salt precipitation

temperature. The examples highlight the importance of frequent inspection and maintenance for heat tracing and insulation around PRVs. Poor condition of the insulation will prevent the heat tracing from maintaining the set point temperature. PRVs are removed for testing on a regular schedule, and the insulation may not be reinstalled “like new” when the PRVs are returned to service. PRV system heat tracing and insulation should be on a checklist for routine operator inspection to verify that the steam is flowing or that the electric circuits are functional, and that the insulation is intact to ensure the reliability of the PRV installation.

Inert Gas Purge

The example in Figure 2 highlights the limitations of steam tracing for preventing PRV plugging if the tracing and insulation are not routinely inspected and maintained or if a robust heat tracing solution is not practical. For added protection the refinery decided to implement an inert gas purge from the PRV inlet back through the SWS process to eliminate the stagnant zone at the PRV inlet that allow the accumulation of reactive vapors. The inert gas purge may be nitrogen, steam, or natural gas, depending on process compatibility. Steam purges are common on instrument connections and nozzles in molten sulfur service and could be extended to PRV inlets.

The gas purge may be set and adjusted using a rotameter, or a flow switch could be used as an indicator that the flow has stopped. A purge rate equivalent to 0.1 to 1 fps gas velocity in the PRV inlet piping should be enough to prevent accumulation of reactive vapors. As with heat tracing and insulation, regular inspection and maintenance of the flow is critical to ensure that the purge mechanism is functioning. The rotameter or flow switch should be on a checklist for routine operator inspection to ensure the reliability of the PRV installation.

PRV Selections to Consider for Solids Prone Systems

A balanced-bellows-type PRV may be a better choice than a conventional PRV because the bellows isolates the spring and other valve parts from the process fluids and potential solids on the discharge side. Many conventional valves can be inexpensively converted with a bellows kit installed by a certified repair shop or by the manufacturer.

Generally, pilot-operated valves are not recommended for services where plugging may occur, and the valve manufacturer should be consulted if selected for this service. When pilot valves are installed in locations where hydrates or solids can form, a non-flowing pilot-operated type is generally recommended to reduce the possibility of hydrate or ice formation (API 520-1 4.2.2.3.3 10th ed., 2020). Purge systems may be required for sensing lines to avoid plugging (API 520-2 7.3.9(g), 7th ed., 2020).

Rupture disks may be installed upstream and/or downstream of a PRV to protect it from the process fluids. These may be useful in situations where solids cause the valve to stick closed, however the application should be carefully considered. Installation of a rupture disk will reduce the PRV installation capacity and increase piping pressure drop.

100% spare PRVs may be installed in parallel to allow for more frequent inspections and maintenance without shutting down the process. A leaking, plugged, or stuck PRV will not perform its function and may only be discovered through inspection and testing. PRV inlet and outlet isolation valves must be positively controlled through the proper application of

administrative controls in conformance with the ASME BPVC and local jurisdictions (API 520-2 8.2, 7th ed., 2020). It is the responsibility of the owner to be sure sufficient written procedures, training, audits, and operating experience are in place to rely on administrative controls.

PRVs with capacity well-matched to the required relief load will achieve velocities that sweep solids away in the discharge piping. A multiple-valve installation may better handle smaller relief loads in the smaller PRV. Some PRV designs have a conversion option to restrict the travel or lift when the valve opens. The valve's capacity may be reduced to as little as 30% of rated capacity. The valve will have the same body but a reduced flow capacity because of the restricted lift. Restricting the lift is a potentially low-cost option and is accomplished by installing a limit washer in the existing valve designed to achieve a specific capacity. This solution more closely matches the PRV rated capacity to the required relief load.

Ensure that the normal operating pressure is sufficiently below the reseating pressure to avoid simmering in flashing-liquid relief cases that can cause hydrates and ice to build up downstream of the PRV (e.g., light hydrocarbons and water). This is especially important for PRVs that are sized for vapor relief (e.g., the fire case) but also may relieve flashing-liquid under another relief case. The reseating pressure after liquid relief may be a lower pressure than for vapor relief and should be checked with the valve manufacturer.

Safety Instrumented System (SIS)

When a PRV is not a reliable choice due to a service prone to solids formation, consider the use of a Safety Instrumented System (SIS), also called a High-Integrity Protection System (HIPS), in lieu of a PRV to eliminate the relief case for the PRV or to reduce the likelihood of discharge. An SIS is essentially a control system separate from the basic control system that runs the rest of the facility. The SIS's major function is to reliably execute automated shutdowns that have a high safety impact and are instrumented and tested such that they are as reliable as a mechanical device such as a PRV.

Case Studies

Following are summaries of three case studies that involve plugging or avoidance of plugging in PRV systems.

Case Study I. Sour Water Strippers (SWS)

Three photos of plugged PRV inlets in SWS service were provided above in the "Reaction Products" subsection. Two of those examples will be described in more detail in this Case Study.

The large gulf coast refinery experienced plugging in the inlet piping of a PRV on the sour water stripper. A photograph of the flange on the PRV inlet spool piece was provided in Figure 2. The plug was discovered during routine maintenance, not because it failed to relieve when needed. The yellow material plugging the spool piece has the appearance of elemental sulfur. Additional investigation led to the finding that the bulk of the solid material most likely was ammonium bisulfide formed from a gas-phase reaction of ammonia (NH_3) with H_2S that was present in the sour water. The refinery installed a nitrogen purge on the PRV inlet line as a secondary protective measure to heat trace and insulation to prevent the accumulation of NH_3 and H_2S vapors and consequently prevent the formation of the solid salts. As noted in the Practices to Avoid Plugging,

relying on gas purge requires instrumentation and regular inspection to verify that the purge is functioning as designed.

Chevron experienced a similar plugging in the PRV inlet piping on the SWS reflux drum (see photo in Figure 3) in one of their refineries. The plugging was discovered when the system pressure increased to slightly above the PRV set point without relieving. The SWS was shut down to investigate the cause of the PRV failing to lift. The solid material was determined to be either ammonium carbonate or ammonium bisulfide. Chevron also has observed plugging in the vapor leg of the level transmitters on SWS reflux drums where similar chemistry exists, which is an indication that the PRV inlet plugging is not an anomaly. The PRV inlet line was steam traced, but the tracing was found to be inoperative. Chevron decided to re-implement the heat tracing to prevent the formation of solid salts in the PRV inlet piping. As noted in the Practices to Avoid Plugging, relying on heat tracing requires regular inspection and maintenance to verify that the heat tracing is functioning as designed.

Case Study II. Hydrates in Natural Gas Liquids (NGL) Treating System

Trimeric has experience with a PRV in a NGL treating system that failed to operate properly during an overpressure event. The NGL treating system consisted of two vessels, each of which was equipped with a PRV. The system contained light hydrocarbons, caustic solution, water, and possibly trace hydrogen sulfide (H₂S), which is an ideal combination for forming hydrates at the cold temperatures resulting from JT expansion across the PRV. The system was effectively isolated during a system shutdown, which made it susceptible to increased pressure generated by thermal expansion. Approximately six days after the shutdown, an operator noticed on a field instrument that the pressure in the NGL treating system had just crossed the PRV set pressure and was continuing to increase. The operator was able to prevent damage to the vessel by venting to the flare header through the PRV bypass line. The operations team did not routinely check the pressures in the treating vessels, because the system was shut down.

Process data collected from the overpressure event and for the 6-day period since the shutdown indicated that there almost certainly were multiple, small-volume relief events due to thermal expansion. The cause of the thermal expansion could have been higher-than-normal ambient temperatures during the day and/or heating from circulation pumps that continued to operate with no net flow through the system to carry the heat away. The recorded vessel pressures peaked numerous times just above PRV set pressure but never approached 10% overpressure until the event. During the two days before the event, the vessel pressure reduction did not fall below 80% of set pressure, and on the final day the pressure hovered near set pressure then increased until the operator intervened to vent the pressure. Consultation with the PRV manufacturer confirmed that the valve would have opened at set pressure and based on the valve characteristics would have relieved a small amount, apparently enough to reduce the pressure and without popping the PRV full open (full lift is required at 10% overpressure). For liquid service, the PRV reseating pressure was 20% below set pressure. During the final two days of high-pressure excursions, the recorded pressure was never reduced to below the reseating pressure. The conclusion was that the PRV “simmered”, opening at set pressure but not fully reclosing, and discharged intermittent small amounts of wet NGL which flashed across the PRV and cooled to form hydrates and ice in the PRV outlet and/or piping to the point that it plugged and could no longer flow. The amount of material relieved during the thermal relief events was too small to be detected on the flare header

pressure indicator. In short, there was no clear indication of the thermal relief events that would have been obvious to the operations team without a close examination of the process data.

The most likely cause of the failure to relieve was plugging due to hydrate or water-ice formation in the outlet piping due to PRV “simmering” from the earlier small relief in the days leading up to the PRV failure. The facility was not able to confirm that hydrates and/or ice were the cause because the conditions were such that the hydrates would have evaporated by the time the PRV was removed from service for inspection and repair. No solids or other physical obstructions were noted when the PRV was taken out of service for testing after the event. One of the PRVs was a conventional type that is susceptible to ice formation around the spring that can prevent the PRV from opening.

The formation of solid hydrates or ice in the PRV outlet piping would not have been applicable for the fire sizing case. The PRV would be fully open in the fire scenario with high velocity in the exit pipe to sweep away any potential solids that formed. A higher PRV inlet temperature caused by heat input from the fire would keep the PRV discharge fluids cooled by the JT effect above hydrate formation and freezing temperatures. The thermal expansion and other smaller flashing-liquid relief cases had not been evaluated in the system design. Consideration of the thermal expansion relief case during the system design may have led to the identification of the JT cooling as a potential issue.

The facility decided to eliminate the potential for hydrate formation by modifying the procedures for system shutdown. The water is removed from the NGL treater to limit the mass of hydrates or ice that could form to only that dissolved in the NGL (i.e., too little to plug the PRV or outlet piping) and to stop the circulating pumps that may have been heating the fluid and causing thermal expansion. Additional evaluation is ongoing to determine if heat tracing is required on the PRV, inlet, and outlet piping to eliminate entirely the hydrate and/or ice formation potential.

Case Study III. High-Pressure Carbon Dioxide Systems (CO₂)

Following is a partial list of general best practices based on Trimeric’s process knowledge in this area for vent system design from CO₂ systems at high pressure, including supercritical pressure, that may also be considered for PRV discharge piping. The recommendations are based on Trimeric’s CO₂ project experience and engineering judgement. There is not a specific standard or guidance document for the design of CO₂ vent systems. The process conditions downstream of the PRV will need to be determined on a case-by-case basis by process simulation modeling using a property package appropriate for the supercritical starting conditions. An approach that Exxon developed for handling PRV venting from CO₂-containing streams was presented at the 2016 LRGCC.

- Select appropriate materials of construction for vent valve and piping to handle the low temperature of the vent condition. Generally, carbon steel or low-temperature carbon steel will not have adequate low-temperature rating. Stainless steel will be required.
- Maintain the vent conditions so as to not form dry ice in the vent piping. The pressure of the vent system may be increased to avoid the formation of dry ice. The valve to let down from the intermediate vent header pressure to atmospheric pressure may be located at the end of the discharge pipe.

- If there is potential for solids in the vent piping, limit potential for plugs using short straight lengths (e.g., fewer than 20 pipe diameters with no turns, elbows, tees, or other restrictions), or remove the vent piping altogether and take appropriate precautions to keep personnel and other equipment out of the direct path of the flow issuing from the vent. It is common in CO₂ service to have relief valves and pressure control valves venting directly to the atmosphere with no vent piping.

Conclusion

Freezing, hydrate and/or ice formation, reaction products, precipitation, non-steady state operations, and solids entrainment are all situations or mechanisms by which solid may be formed and lead to plugging of a PRV and its inlet and outlet piping. Gas conditioning applications that have the potential – and history – for plugging PRVs include sour water strippers, caustic scrubbers, CO₂ systems, and wet NGL/ light hydrocarbon handling. Practices to avoid PRV plugging were identified, and include heat tracing and insulation, inert gas purges, PRV selections, and safety instrumented systems.

Acknowledgments

Trimeric acknowledges the contributions of Chevron for photos and discussions to provide background information on PRV plugging in sour water stripper service.

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