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Successful Demonstration of Relieving CO_2-Solid-Forming Streams through a Pressure Relief System

Mary Kay O'Connor Process Safety Center International Symposium
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Abstract

The demand for natural gas, considered the cleanest burning hydrocarbon fuel available, is expected to rise significantly over the foreseeable future. However, natural gas produced from many major reservoirs can contain significant amounts of carbon dioxide (CO_2) and must be treated before it can be used as an environmentally acceptable fuel. These treatment processes often require high-pressure operations forming highly concentrated CO_2-rich streams.

Pressure protection for these systems has been challenging to date because of the potential for solids generation upon pressure let down and the consequent potential for plugging that the solids present.

ExxonMobil has completed successful field demonstrations relieving dehydrated, CO_2-rich liquid and vapor streams forming up to 40 wt% solids in relief lines. The results of these field demonstration tests as well as learnings from design of CO_2-solid-forming relief systems are discussed in this paper.

Introduction

ExxonMobil anticipates total global energy demand to grow 35% by 2040 relative to 2010[1]. The clean burning characteristics of natural gas and its lower greenhouse gas footprint make it particularly attractive in electrical power generation which will provide a significant portion of the energy demand growth. Natural gas emits up to 60 percent less carbon dioxide (CO_2) than coal when generating electricity, which can become quite significant if costs start rising due to the implementation of policies designed to reduce greenhouse gas emissions.

However, natural gas produced from many major reservoirs can contain significant amounts of carbon dioxide (CO_2) and must be treated before it can be used as an environmentally acceptable fuel. These treatment processes often require high-pressure operations forming highly concentrated CO_2-rich streams. Pressure protection for these systems has been challenging to date because of the potential for solids generation upon pressure let down and the consequent potential for plugging that the solids present.

In the past, certain relief scenarios that may result in formation of CO_2 solids in the relief system have been avoided or protected via a High Integrity Pressure Protection System that would prevent the relief scenario from occurring. Installation, operation, and maintenance of these systems can be rather costly, considering the redundant valving, instrumentation and controls involved and their frequent and rigorous testing. The ability for conventional pressure relief mechanisms to replace these complex systems, when there is a potential for solid CO_2 generation during relief, could save significant capital and operating expenses.

In a safety relief event, solid CO_2 particles could be generated as the high CO_2 content mixture experiences Joule-Thomson cooling in the relief device due to rapid adiabatic expansion. To test the tendency for blockage due to solid CO_2 particles, ExxonMobil conducted a series of commercial-scale experiments across a wide range of fluid compositions, temperatures, relief pressures, and relief systems. In these tests, gas and liquid mixtures of carbon dioxide and methane (CH_4) with trace amounts of nitrogen (N_2) were rapidly expanded through PSVs, and signs of line plugging from solid CO_2 were investigated. From these tests, important design parameters were identified that can prevent solid CO_2 plugging and allow the relief of solid CO_2-forming fluids.

Experiment Summary

A series of experiments were conducted to test the effect of gas composition, flow rate, CO_2 solids mass fraction, and vent line geometry on the tendency to form a restriction during a pressure relief process. All tests were performed at a demonstration facility within the ExxonMobil's Shute Creek Treating Facility (SCTF) near LaBarge, WY.

Two main groups of tests were conducted:

Group #	CO_2 Composition	CH_4 Composition	Relief Phase	Solids Generation
1	~20%	~80%	Superheated Vapor	Approximately 5 wt%
2	~80%	~20%	Saturated Liquid	Approximately 48 wt%

Product-quality CH_4 and CO_2 streams were blended together, as necessary, to provide the tested feed concentration. Each inlet stream was dried in a molecular sieve and filtered to remove contaminants. A residual concentration of nitrogen was present in all tests, up to a concentration of approximately 1%.

Solid CO_2 Behavior

Phase Behavior

When CO_2 or mixtures of CO_2 and CH_4 are depressured across a safety relief valve, solid CO_2 particles could be generated due to Joule-Thomson cooling and a shift in the phase diagram. The fraction of solids formed is dependent on primarily fluid composition, upstream temperature and pressure, and downstream pressure.

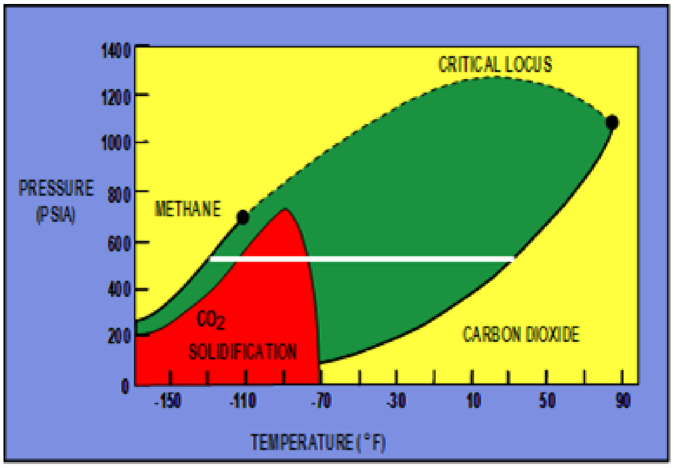


Figure 1. Methane-Carbon Dioxide P-T Diagram

Figure 1 depicts the P-T phase diagram for CO_2 and CH_4 mixtures, with bounds shown by the pure components. A CO_2 solidification dome, which represents a Vapor-Solid equilibrium, occupies a large fraction of the typical Vapor-Liquid equilibrium region at pressures below approximately 700 psia. In a relief event, streams will typically relieve through a PSV from high pressure, in the green Vapor-Liquid Equilibrium (VLE) region, to low pressures, sometimes entering into the red CO_2 solidification region. A typical flare header design pressure is 225 psig, which is the design pressure for stainless steel ANSI 150# flanges in cold, cryogenic services.

The formation of solids in the flare header raises the concern that these solids may accumulate and form a blockage in the piping. A blocked-flow event in the flare piping could cause pressure to build up beyond the design pressure of the piping, leading to an overpressure, and potentially a loss of containment event. The objective of the PSV relief tests was to identify if the formation of solids would lead to any blockages or overpressure scenarios.

Before reviewing the results of the tests it is important to understand what happens to a fluid as the pressure is reduced across the PSV. For illustrating purposes, Figure 2 below shows a P-H diagram for **pure CO_2** with each phase region highlighted in order to facilitate following the behavior of pure CO_2 during pressure relief.

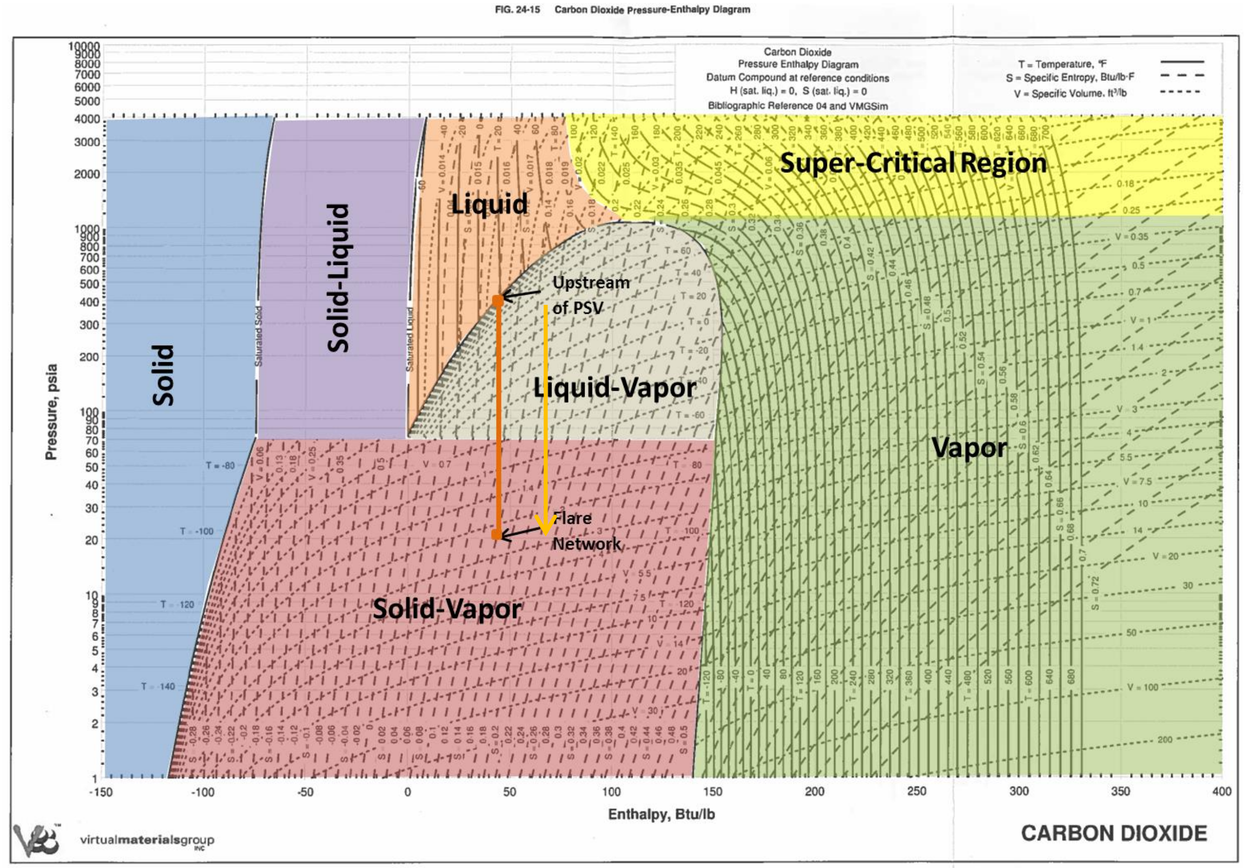


Figure 2. Pure Carbon Dioxide P-H Phase Diagram

The pressure relief across a PSV may pass through isentropic and isenthalpic regimes. For the purpose of this study, the relief across a PSV was modeled as an isenthalpic flash. In other words the enthalpy remains constant throughout the relief event. The orange line in the diagram indicates a representative relief path for a saturated, pure CO_2 liquid at 400 psia, 20°F that flashes into a relief line at 20 psia. When depressuring a stream of pure, liquid CO_2 the liquid begins to vaporize as it enters into the Liquid-Vapor Equilibrium region. At ~70 psia, solid CO_2 particles form as the fluid enters into a Solid-Vapor equilibrium. The fluid remains in the solid-vapor region as the pressure continues to fall to atmospheric pressure. Upon reaching atmospheric pressure, 14.7 psia, the temperature could drop to approximately -110°F.

For **pure CO_2 systems** undergoing depressurization, solids do not form until approximately 70 psia is reached in a conventional relief event in which the relieving fluid is liquid and/or vapor. However, if after dropping below 70 psia, solids were to build up in a relief line for a **pure CO_2 system,** and cause backpressure on the flare header, the system would enter back into the Vapor-Liquid Equilibrium region, as the pressure would rise again above 70 psia. One will note that for **pure CO_2** systems, this pressure is below the typical 225 psig design pressure of stainless steel ANSI 150# flanges in cold, cryogenic service. However, the presence of CH_4 in a multicomponent CO_2-CH_4 mixture raises the CO_2 frost point pressure, and lowers its temperatures.

Not only does the phase diagram shift to significantly colder temperatures with the presence of methane, but the phase envelope opens up with the presence of this second component – that is the solidification conditions broaden. It should also be pointed out that all indications are the solid generated in these CH_4-CO_2 mixtures at these conditions are pure CO_2 such that all CH_4 remains in the vapor or liquid phase.

To approximate the behavior of the two sets of relief tests, P-T and P-H diagrams are presented below at the two test compositions. Figures 3 to 6 were generated using the Peng Robinson Equation of State with a commercial simulating tool with the ability to model vapor-liquid-solid equilibrium and predict weight fractions of CO_2 solids.

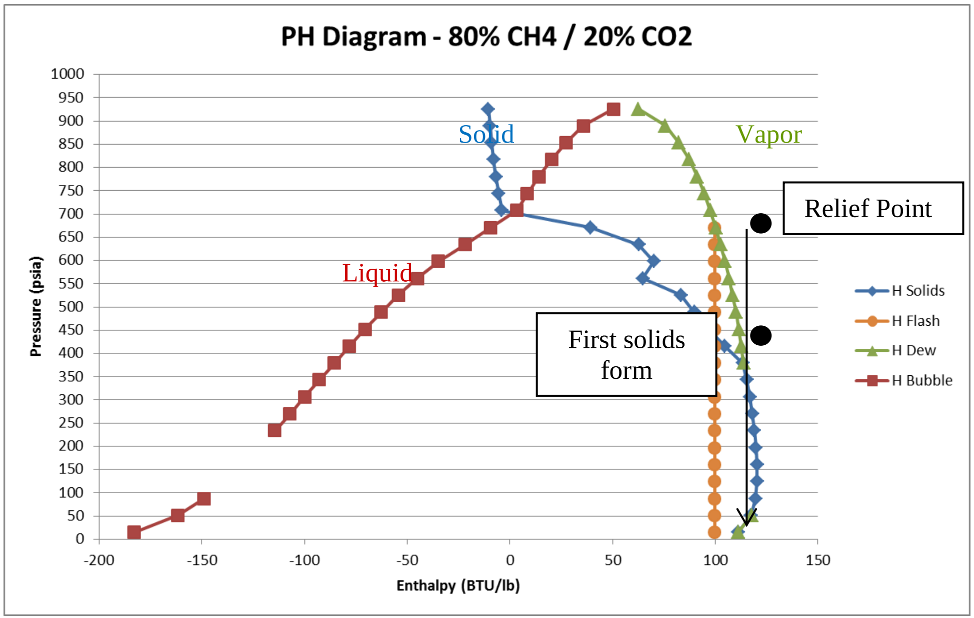


Figure 3. P-H Diagram of 80% CH4 / 20% CO2 Mixture

The first set of tests relieved a slightly superheated vapor mixture of approximately 80% CH_4 / 20% CO_2 at 640 psia. The path of the representative isenthalpic flash across the PSV is depicted in orange, with the dew point curve in green and bubble point curve in red. The blue curve indicates the frost point, or the point at which solid CO_2 first forms. With the addition of CH_4

the pressure at which solid forms increases significantly compared to the pure CO2 example given above. In this case the relief path passes the frost point at approximately 450 psia, and the mixture stays in Solid-Vapor equilibrium throughout the low pressure flare header.

It is also helpful to understand how the temperature is changing across the flare header as shown in Figure 4 below.

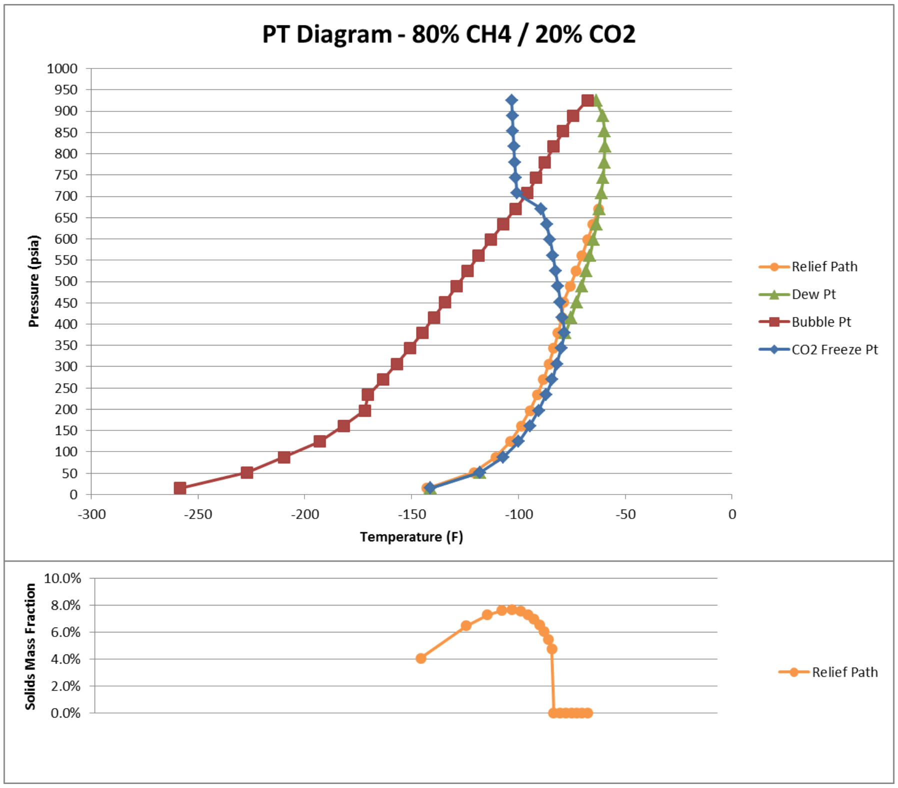


Figure 4. P-T Diagram of 80% CH4 / 20% CO2 Mixture

The relief starts at the dew point at 650 psia, and the pressure and temperature decreases steadily as the stream passes through the Vapor-Liquid region, until the CO_2 solidification line is crossed. During the formation of the solid CO_2, little temperature change occurs since the latent heat is the dominant energetic mechanism (this is easier to see in Figure 6 than Figure 4). At low flare header pressures the temperature drops significantly across a small pressure range. It is important to consider this reduction in temperature at the lower pressures when designing the flare header, especially for material selection at the cryogenic temperatures.

The secondary plot at the bottom of Figure 4, demonstrates the mass fraction of solids at each point on the relief path curve above. Solids have the ability to form up to ~8 wt% in the flare header for this relief path. The formation of solid CO_2 behaves as a step change across the solidification curve. It is not a gradual buildup to a large fraction of solids but instead forms across a very small temperature and pressure range.

P-T, P-H, and solids formation curves are presented in Figures 5 and 6 below for the ~80% CO2 / 20% CH4 mixtures at bubble point conditions at 660 psia.

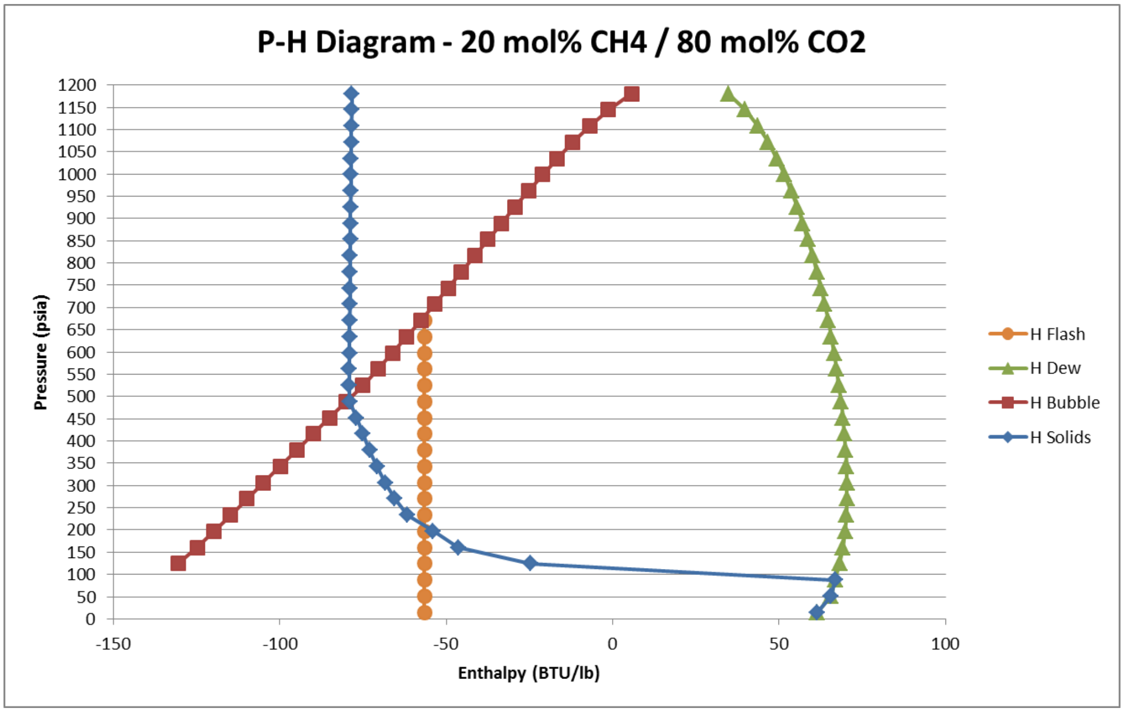


Figure 5. P-H Diagram of 20% CH4 / 80% CO2 Mixture

The path of the representative isenthalpic flash across the PSV is depicted in orange. At the lower concentration of CH_4 than in the Vapor Relief Test (20% here vs. 80% in the vapor test), the pressure at which solid first forms decreases from approximately 450 psia to approximately 200 psia. Thereafter, the mixture again stays in Solid-Vapor equilibrium throughout the low pressure flare header.

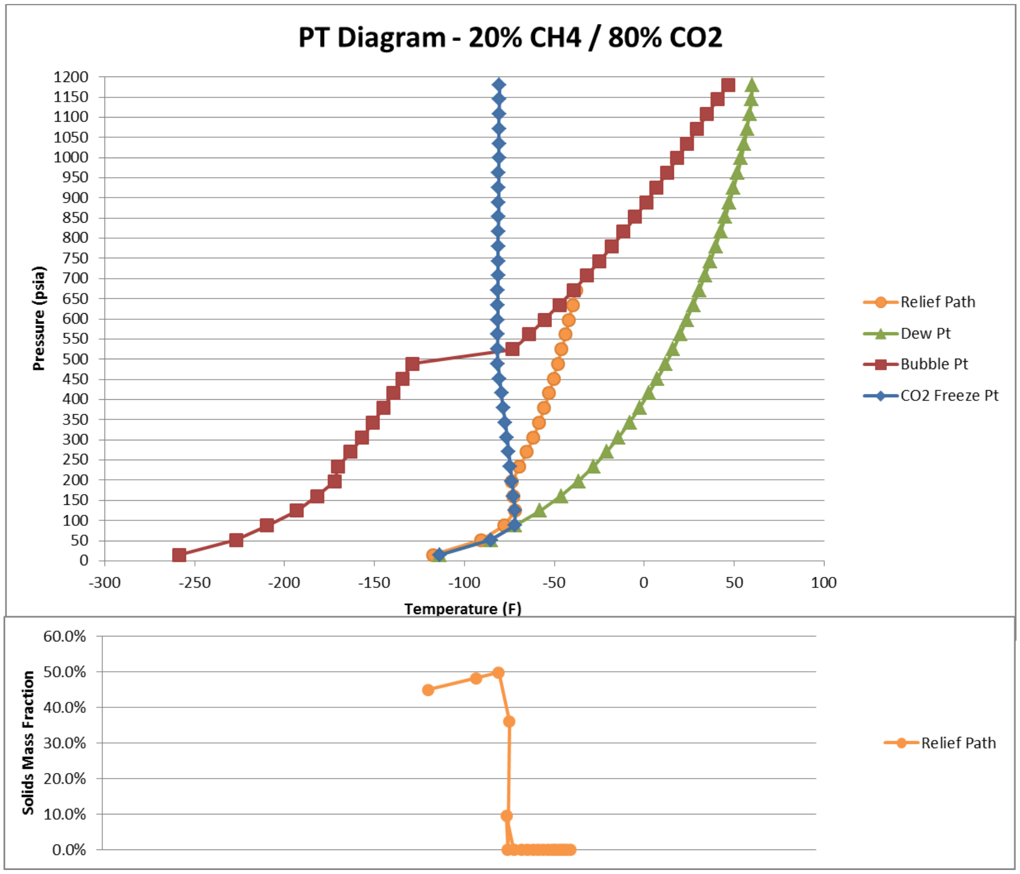


Figure 6. P-T Diagram of 20% CH4 / 80% CO2 Mixture

Figure 6 demonstrates the P-T diagram and relief path of the bubble point mixtures. Although the temperatures of the mixture are higher for the 80% CO2 / 20% CH4 case than the 20% CO2 / 80% CH4 case, the solids fraction is still much higher because of the high fraction of CO_2 in the stream. During the phase change into solids, the temperature follows the path of the blue solidification curve since only latent heat is the driving force. Again, the temperature drops significantly at the low pressures of the flare header across a small pressure range.

There is not a slow buildup of solids after the relief path crosses the solid CO_2 formation curve. In both cases the formation of solid CO_2 occurs across a very small pressure range.

Mechanism of Solid CO_2 Accumulation

The flow-blocking behavior of solid CO_2 in the relief piping was the primary element under investigation during this study. Efforts were also devoted to better understanding the morphology of, and mechanisms for the formation and accumulation of solid CO_2 under these and other conditions of interest. In general there appear to be two main mechanisms by which solid CO_2 particles may accumulate, and prior to the testing it was unknown the degree to which accumulation would pose an issue.

The first mechanism can be thought of as a heterogeneous nucleation, or adherence of solid CO_2 on the pipe walls. The solid CO_2 particles, largely as individual particles, adhere to the wall of the piping or build up upon a pre-existing “mound” of solid CO_2. The roughness of the internal walls of the piping, bends, elbows and rising segments in the piping may provide just enough cause for the CO_2 particles to deposit and accumulate. Additional CO_2 particles may then build up on top of the initial particles and contribute to larger accumulations of solids. One can think of this phenomenon as analogous to sand particles building up inside a pipe. The sand starts to “stick” to the wall, which causes more sand to get “caught” and build up a larger mound of sand over time.

The second mechanism can be thought of as a homogeneous nucleation, or agglomeration of CO_2 particles. Solid CO_2 particles have a much greater interaction with each other and forge a stronger bond than simply piling on top of other CO_2 particles like hard spheres. Consider the difference between ice and snow. Both are made of solid H_2O particles, but snow is a loose collection of particles of solid H_2O, behaving more analogously to sand, whereas ice packs those solids particles into a tight crystalline structure which becomes much harder to break apart.

If the solid CO_2 produced during a release were of the first kind there would be a very good chance it could be fluidized and moved thru the relief piping without much consequence. If it were of the second kind, it could be more difficult to deal with and could lead to the build up of sufficiently large blocks of strong structures, in turn causing a blockage and an overpressure in the piping.

Preventing Solids Accumulations

There are three main factors that make accumulation of solid CO_2 difficult: Velocity, Pressure, and relief system design/geometry.

The high velocity of the gas in the flare header can help entrain solids, carrying them through the relief system, and prevent them from accumulating on the pipe walls. Although the relieving vapor is less dense at lower flare header pressure than the higher relief pressure, the overall density of the fluid in the relief piping may be inflated given that the solid CO_2 that forms is inherently a dense material. This may keep velocities in relief piping low in applications with significant fractions of solid CO_2 form. When all is taken into consideration, if the gas velocity is high enough, it will entrain the solids and largely prevent them from building blockages.

Should solid CO_2 deposit and accumulate, causing a restriction or plugging of the line, pressure would build up in the line, potentially leading to an overpressure scenario. However, the restriction or plug would have to withstand the significant upstream pressure pushing on the plug with enough force to likely break up its solid structural formation. Most low pressure, cryogenic flare header systems are composed of stainless steel ANSI 150# flanges which have a design pressure of around 225 psig at cryogenic temperatures. This means that if a solid accumulation occurs and pressure starts to build, there will be a significant pressure pushing on the potential blockage before the pipe ever gets overpressured.

The smallest outlet piping, and thus worst case size, that meets API 526 is 2” piping, which is the primary size of the relief piping tested in this study. For 2” piping the 225 psig pressure would correlate to a point force of approximately 750 lbf on the solid CO_2 plug at the time of overpressure, assuming the solid was able to bridge across the entire cross-section of the 2” line. For a solid accumulation to plug the piping, the binding mechanism for solid buildup would have to be very strong to withstand this force. In larger piping, this force would increase significantly, by the square of the radius, making it even easier to break apart any solid CO_2 buildup.

A final piece that helps prevent solid CO_2 buildup is designing the piping in such a way that eliminates pipe segments that would promote solid buildup. For example, sharp turns, contractions in the piping, and vertical rises in the slope of the piping may promote the buildup of solids. As will be discussed in the next section, each of these piping design factors was tested during these commercial-scale experiments.

Experimental Setup and Procedure

PSV

A pilot-operated, 1”x2” PSV with a 0.205 in^2 orifice was utilized for both sets of tests.

During the vapor relief tests, a non-modulating, pop action pilot was used. The non-modulating lift is designed to move to 100% open with minimal overpressure. The effect of a pop action valve is that the PSV lift, and thus the relieving flowrate, rises rapidly to 100%. The pop action valve was thought to help prevent solid plugging by quickly moving to full flow through the PSV and reducing the flow buildup time in which a low flow rate may promote the buildup of solids. This is a “non-flowing” type of pilot, so there was no concern of CO_2 forming in the pilot itself.

After the pop action pilot was successful for the vapor relief tests, the pilot was replaced with a modulating pilot for the entirety of the liquid relief tests. The facility was not set up to provide a high enough liquid flow rate to support the valve at 100% lift without de-inventorying the liquid supply in under the 20-minute allotted time period, so the maximum lift of the valve was restricted to limit the flowrate through the valve. This was performed by tightening a nut which limited the maximum lift at approximately 50%. A corresponding 50% capacity reduction of the PSV was anticipated. This was also a “non-flowing” type of pilot, so there was no concern of CO_2 forming in the pilot itself.

PSV Test Loop

The arrangement of the piping downstream of the PSV is pictured in Figure 7 below. All piping in the test loop set-up was rated, tested, and protected for 825 psig (higher than the 650 psig test PSV set pressure). This ensured that if CO_2 solids did plug the piping, there would not be an over-pressure event.

The 2” stainless steel relief piping was intended to follow a “tortuous path” to demonstrate a “worst case relief piping arrangement.” It contained the following characteristics that would theoretically promote solid buildup:

- The 2” relief piping corresponded to the smallest commercial PSV outlet size that meets API 526. As discussed above, smaller piping could promote the ability of solids to “bridge” across the piping.

- Contained four (4) 90° elbows. Each 90° elbow presents a potential area for solids accumulation, as a local section of low velocity occurs at the bend. A better design may avoid 90° elbows and use softer turn, 45° elbows instead.
- Contained an expansion and contraction to/from 4" piping. The contraction from 4" to 2" provided a sloped surface area which may have promoted solids accumulation. In practice a contraction in a flare line is unusual but is allowed as long as the piping does now swedge down below the outlet flange size of the PSV, per API 526.

A bypass valve, PV-9760, was provided to help line out flows during test setup. It is closed during operation of the PSV.

The outlet of the test PSV fed into a heat exchanger aimed at sublimating the solids before the relieved stream entered the true flare header. There is a temperature-controlled valve at the outlet of the heat exchanger that closed (stop flow) if the exchanger provided insufficient heat (e.g. failure of Heating Medium supply).

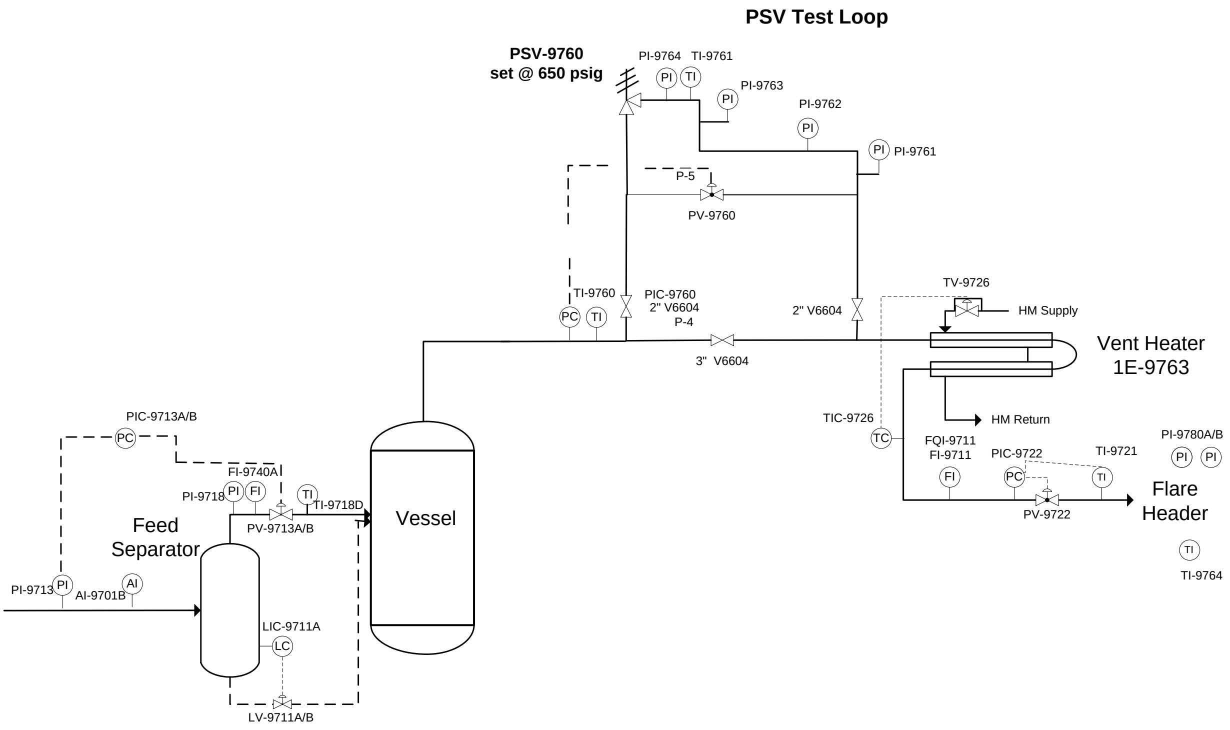


Figure 7. PSV Test Loop Process Flow Diagram

Vapor Relief Tests

Figure 8 below demonstrates the flow path for the vapor relief tests. The CO_2-CH_4 blending and feed chilling units occur upstream of the diagram.

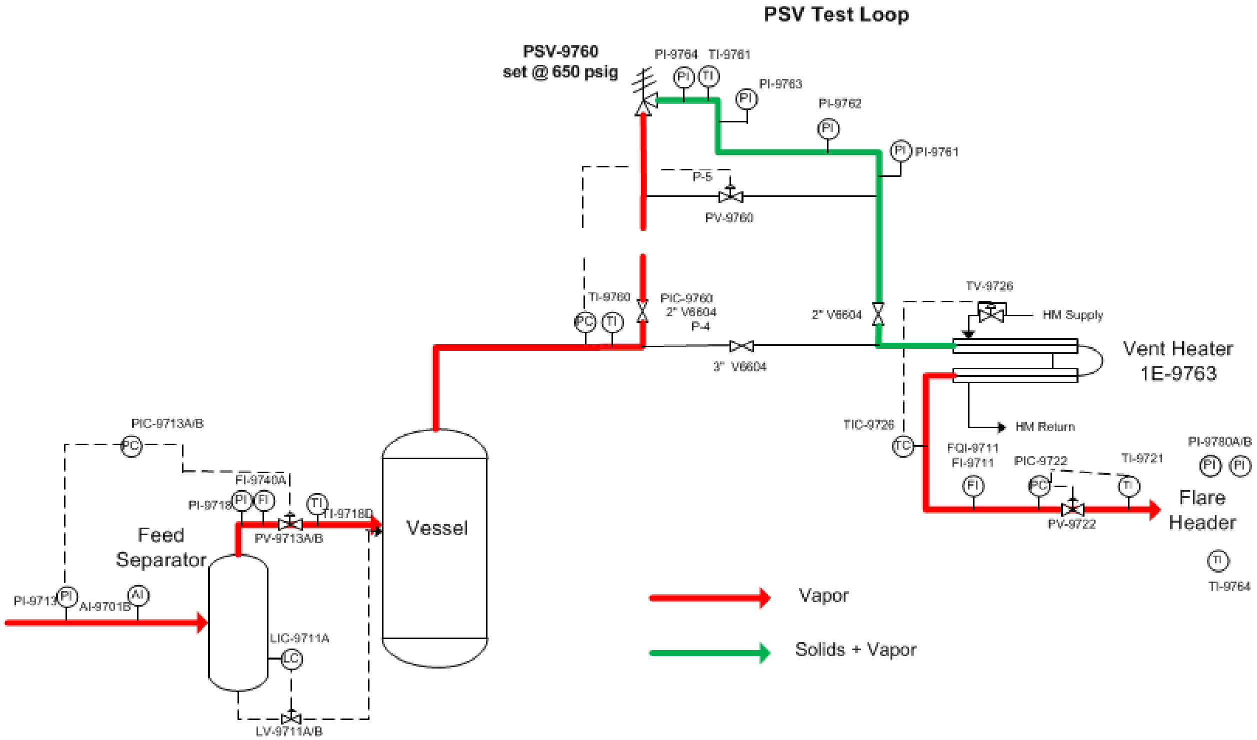


Figure 8. Vapor Relief Test Flow Path

The experimental procedure for the Vapor Relief Tests is given below:

1. Establish CH_4 flow from plant inlet through bypass (PV-9760)
2. Achieve desired test composition by blending CO_2
3. Reduce temperature to approximately -56°F
4. Achieve steady state on pressure, temperature and flow
5. Close test loop bypass and increase inlet flow
6. Build Pressure upstream of PSV
7. PSV lifts at set pressure
8. Maintain inlet flow to keep PSV relieving for a minimum of 12 minutes
9. Shut off test feed flow

In summary, a steady flowrate through the bypass valve, PV-9760, at the desired CH_4 and CO_2 compositions, pressure, and temperatures was achieved before activating the PSV. The bypass valve was closed and the pressure upstream was increased (the feed pressure was from a significantly higher source pressure) until the PSV lifted. The flow through the PSV was maintained for a minimum of 12 minutes, during which solids were formed in the PSV relief path piping and sublimated in the vent heater, 1E-9763. After 12 minutes, inlet flow was shot off, which quickly closed the PSV.

Liquid Relief Tests

Figure 9 below demonstrates the flow pattern for the Liquid Relief Tests.

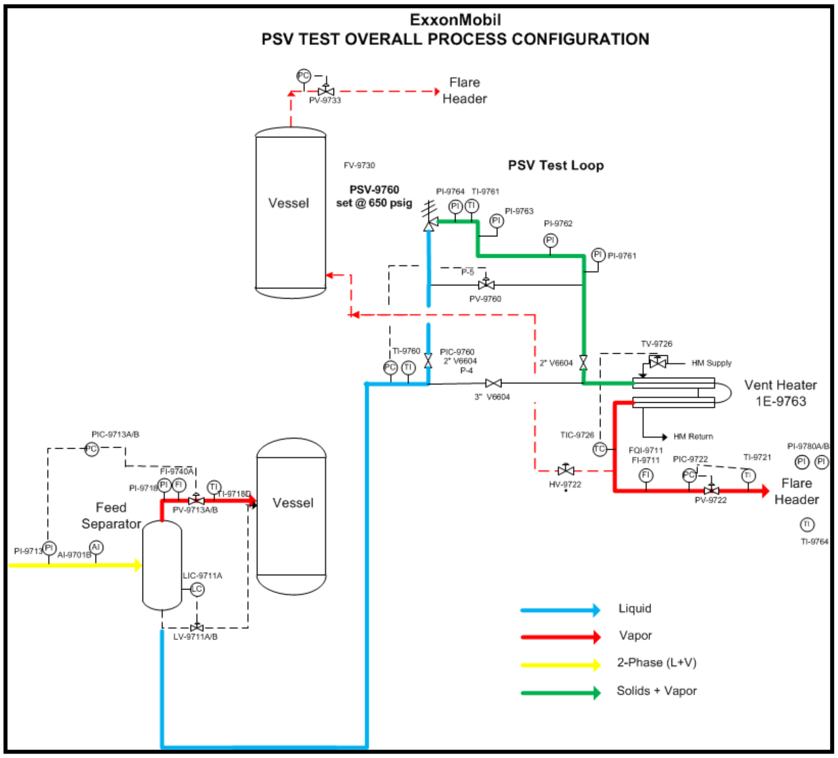


Figure 9. Liquid Relief Test Flow Path

The experimental procedure for the Liquid Relief Tests is shown below:

1. Chilling train outlet targeted at -30 F
a. Note 1: only 75% of the feed stream condenses at this temperature
b. Note 2: Any liquid that condenses has a higher concentration of CO_2 than in the total feed stream
2. Liquid flows out of the bottom of the feed separator through the test PSV bypass valve, PV-9760
3. Vapor accumulates in the feed separator to keep a “bubble” atop the liquid in order to control pressure
4. Excess vapor is directed into a downstream storage vessel. It is flared at the end of the test.
5. Flow through test PSV bypass stopped
6. Feed pressure set point increased to 680 psig
a. Enriches relief liquid with CH4
7. Relief composition approx. 80% CO2, 20% CH4
8. PSV relieves at 660 psia

9. Maintain inlet flow to keep PSV relieving for a minimum of 12 minutes
10. Shut off flow

In summary, a steady liquid flowrate through the bypass valve, PV-9760, at the desired CH_4 and CO_2 compositions, pressure, and temperature was achieved before activating the PSV. A sufficient liquid level in the “Feed Separator” vessel was built to provide a sufficient charge of liquid for the tests. A small vapor pocket was maintained on top of the liquid in the feed separator to act as the driving force to push the liquid through the relief valve. The bypass valve was then closed and the pressure upstream was increased (the feed pressure was from a significantly higher source pressure) until the PSV lifted. The flow through the PSV was maintained for a minimum of 12 minutes, during which solids were formed in the PSV relief path piping and sublimated in the vent heater, 1E-9763. Some of the vaporized relief flow was diverted to a vessel and later routed to flare. Since the PSV had a modulating pilot, the flowrate through the PSV was maintained by holding the upstream pressure as steady as possible. This proved somewhat difficult during test operation and accounts for some of the swings in flowrate and pressures during the testing. After a minimum of 12 minutes, inlet flow was shot off, which quickly closed the PSV.

Test Success Criteria

The following test success criteria were established prior to running the tests:

1. No full blockage of test piping downstream of PSV is observed within 10 minutes of relief. This was representative of a sufficiently long relief duration.
2. Downstream pressure does not exceed 172 psig over a sustained period. This is 75% of design pressure for the ANSI 150# stainless steel flanges at the cryogenic temperatures of these types of flare header applications.
3. Short Term pressure excursions do not exceed 225 psig. This is 100% of design pressure for the ANSI 150# stainless steel flanges at the cryogenic temperatures of these types of flare header applications.

When analyzing the results, steadily increasing pressures in the test section may be interpreted as an indication of restriction. The disparity between consecutive pressure transducers may be used to determine the location of a restriction. Pressure pulses following the release of a restriction may be attributed to the momentum of released solids.

Test Results and Discussion

Baseline 100% Methane Feed

A test was first performed with pure methane vapor to set a baseline for the operation of the PSV and test loop.

The main data points to collect were to confirm PSV relief pressure set point of 660 psia and determine backpressure downstream of PSV. The table below summarizes the test conditions and results of the methane feed test.

Composition	100% Methane Feed (ca. 97% CH_4, 3% N_2)
PSV Inlet Temperature	- 50°F
Relief Pressure	640 psia
PSV Flow Rate	$4*10^6$ scfd (estimated to maintain PSV open during relief)
Test duration	~ 13 minutes
Minimum Temp Downstream of PSV	- 120°F
Backpressure (Pressure Downstream of PSV)	~ 100 psig

Figures 10 to 12 below depict the flowing results from the CH_4 only test.

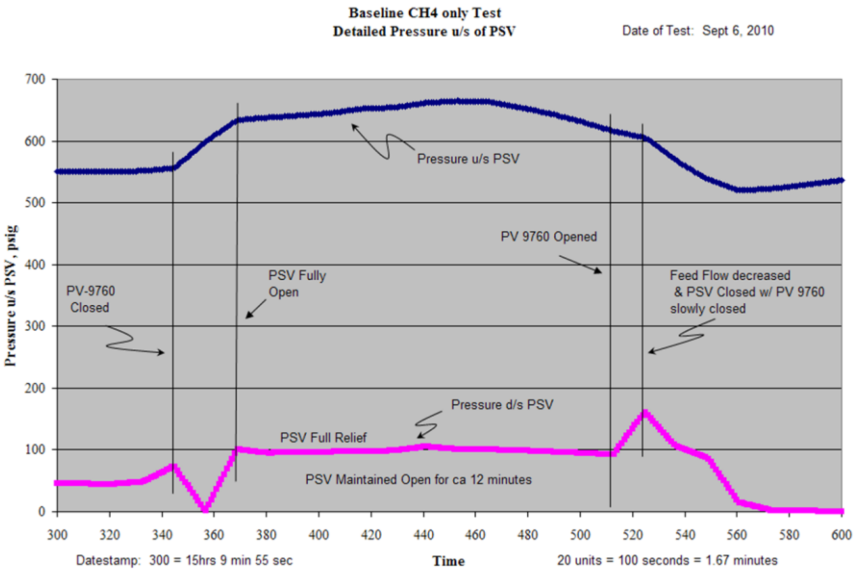


Figure 10. Baseline CH4 Pressure Profile

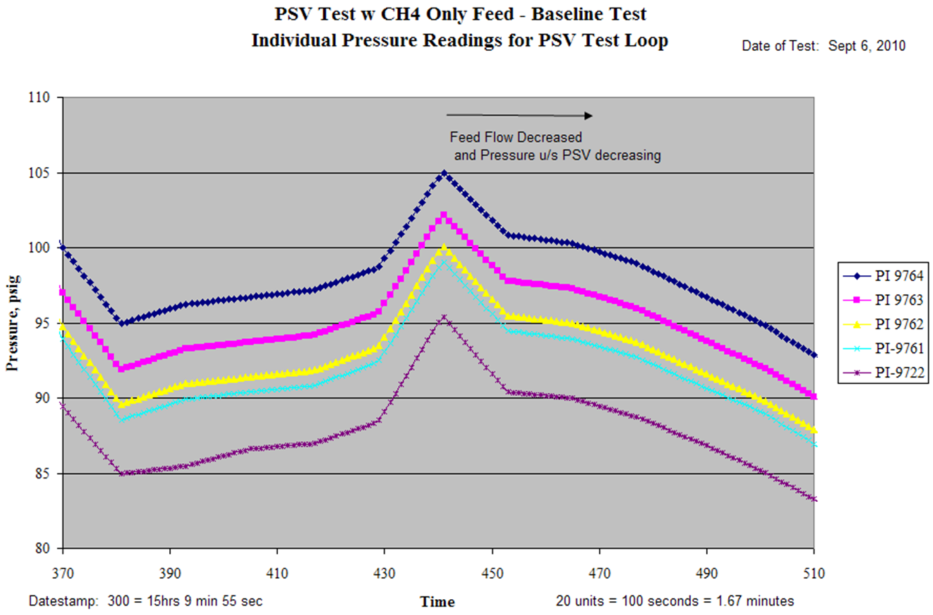


Figure 11. Baseline CH4 Test Individual Pressure Readings for PSV Test Loop

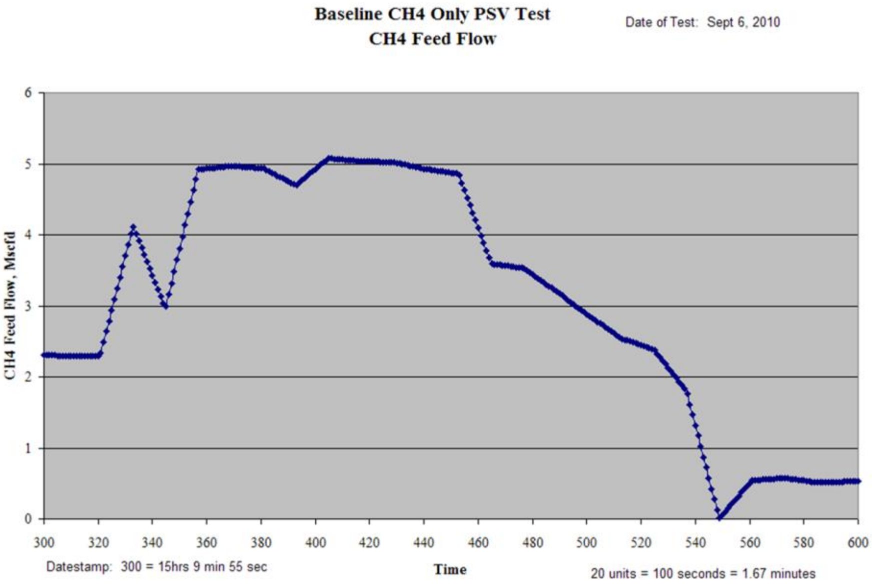
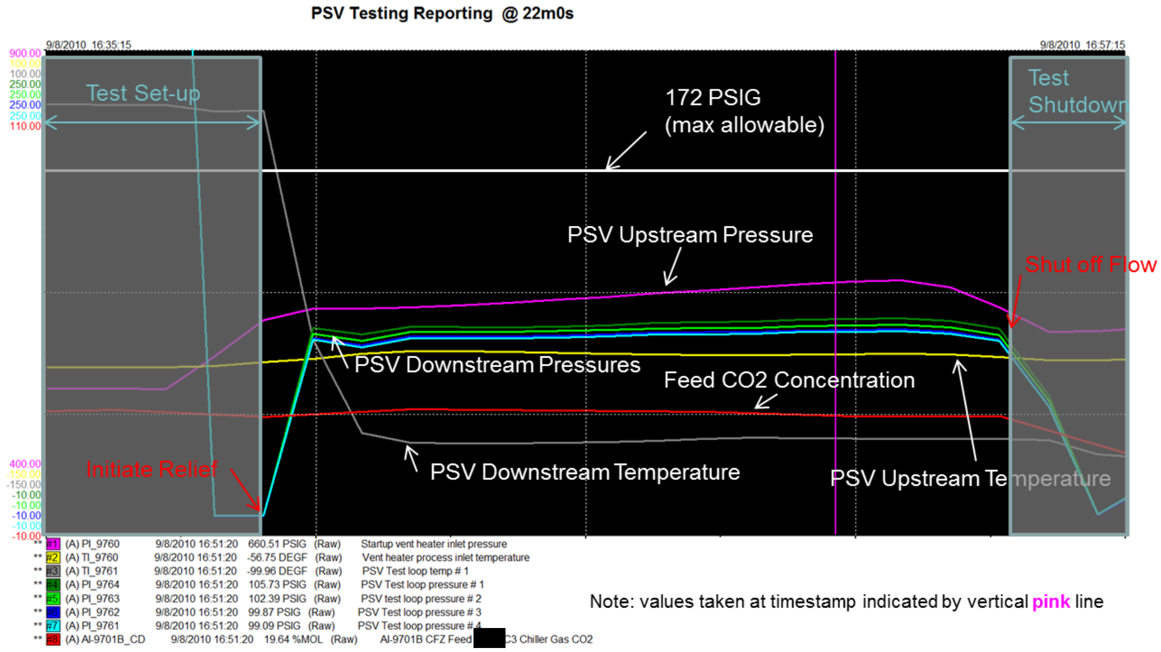


Figure 12. Baseline CH4 Test Feed Flow

The system performed as expected with the CH_4 only test. A steady 10 psi pressure drop was recorded across the multiple pressure transmitters downstream of PSV in the PSV test loop, and the PSV lifted at 640 psia, which is within the range of the correct set pressure.

Vapor Relief Tests

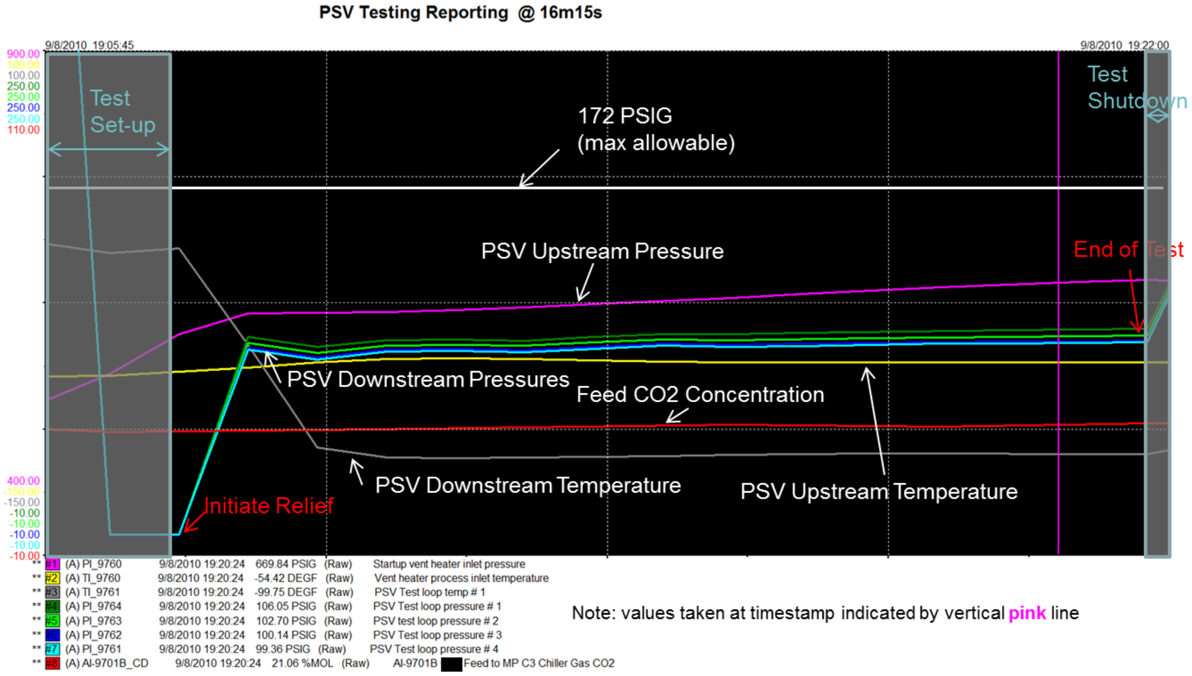
Two Vapor Relief Tests were performed with an approximately 80% CH_4 / 20% CO_2 mixture relieving through the pop action, non-modulating PSV. The objective was to test the backpressure and check for signs of blockage while generating a small amount of solids. In both tests an estimated 5 wt% solids were generated at actual test conditions.



**	#1	(A) PI_9760	9/8/2010 16:51:20	660.51 PSIG	(Raw)	Startup vent heater inlet pressure
**	#2	(A) TI_9760	9/8/2010 16:51:20	-56.75 DEGF	(Raw)	Vent heater process inlet temperature
**	#3	(A) TI_9761	9/8/2010 16:51:20	-99.96 DEGF	(Raw)	PSV Test loop temp # 1
**	#4	(A) PI_9764	9/8/2010 16:51:20	105.73 PSIG	(Raw)	PSV Test loop pressure # 1
**	#5	(A) PI_9763	9/8/2010 16:51:20	102.39 PSIG	(Raw)	PSV test loop pressure # 2
**	#6	(A) PI_9762	9/8/2010 16:51:20	99.87 PSIG	(Raw)	PSV Test loop pressure # 3
**	#7	(A) PI_9761	9/8/2010 16:51:20	99.09 PSIG	(Raw)	PSV Test loop pressure # 4
**	#8	(A) AI-9701B_CD	9/8/2010 16:51:20	19.64 %MOL	(Raw)	AI-9701B CFZ Feed [redacted] C3 Chiller Gas CO2

Note: values taken at timestamp indicated by vertical **pink** line

Figure 13. Vapor Relief Test A Results



**	#1	(A) PI_9760	9/8/2010 19:20:24	669.84 PSIG	(Raw)	Startup vent heater inlet pressure
**	#2	(A) TI_9760	9/8/2010 19:20:24	-54.42 DEGF	(Raw)	Vent heater process inlet temperature
**	#3	(A) TI_9761	9/8/2010 19:20:24	-99.75 DEGF	(Raw)	PSV Test loop temp # 1
**	#4	(A) PI_9764	9/8/2010 19:20:24	106.05 PSIG	(Raw)	PSV Test loop pressure # 1
**	#5	(A) PI_9763	9/8/2010 19:20:24	102.70 PSIG	(Raw)	PSV test loop pressure # 2
**	#6	(A) PI_9762	9/8/2010 19:20:24	100.14 PSIG	(Raw)	PSV Test loop pressure # 3
**	#7	(A) PI_9761	9/8/2010 19:20:24	99.36 PSIG	(Raw)	PSV Test loop pressure # 4
**	#8	(A) AI-9701B_CD	9/8/2010 19:20:24	21.06 %MOL	(Raw)	AI-9701B [redacted] Feed to MP C3 Chiller Gas CO2

Note: values taken at timestamp indicated by vertical **pink** line

Figure 14. Vapor Relief Test B Results

After the PSV lifted, the pressure smoothly rose and steadied out around 100 psig. None of the PSV downstream pressures approached the 172 psig threshold at any time throughout the relief. There was a visible pressure gradient, similar to the CH_4-only baseline test, across the 4 pressure transmitters in the PSV test loop that stayed constant over time, indicating no signs of local blockage inside the relief line. Due to the Joule Thomson cooling from depressuring across the PSV, the downstream PSV temperature reduced gradually until it steadied out around -100°F. During these tests the feed CO_2 concentration and PSV upstream temperature remained steady. A slightly higher inlet rate is provided than can be passed through the PSV, so as a result the pressure upstream of the PSV gradually rose over time.

The system showed no indication of blockage in any of the piping downstream of the PSV for both Vapor Relief Tests. The downstream pressures were constant for the duration of the test and remained under the 172 psig threshold at all times. No pressure spikes were observed over the entire duration of testing. As a result, all tests met the designated acceptance criteria.

Liquid Relief Tests

Three Liquid Relief Tests were performed with a 20% CH_4 / 80% CO_2 mixture relieving through the modulating PSV. The objective was to test the backpressure and check for signs of blockage while generating a significantly higher amount of solids. An estimated 48 wt% solids were generated at actual test conditions.

The graphs below demonstrate the test results for the three Liquid Relief Tests. The values shown at the bottom of the test correlate to the timestamp at the vertical purple line shown on the graphs.

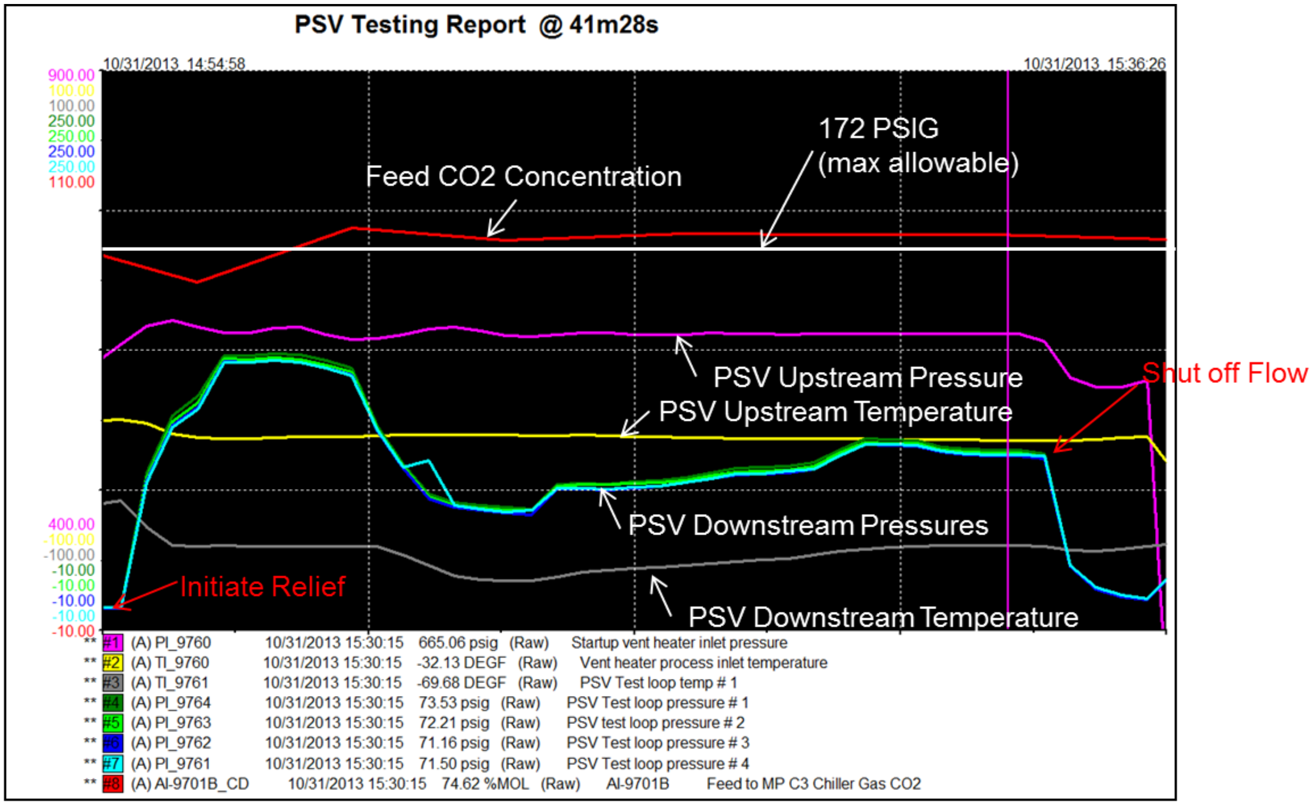
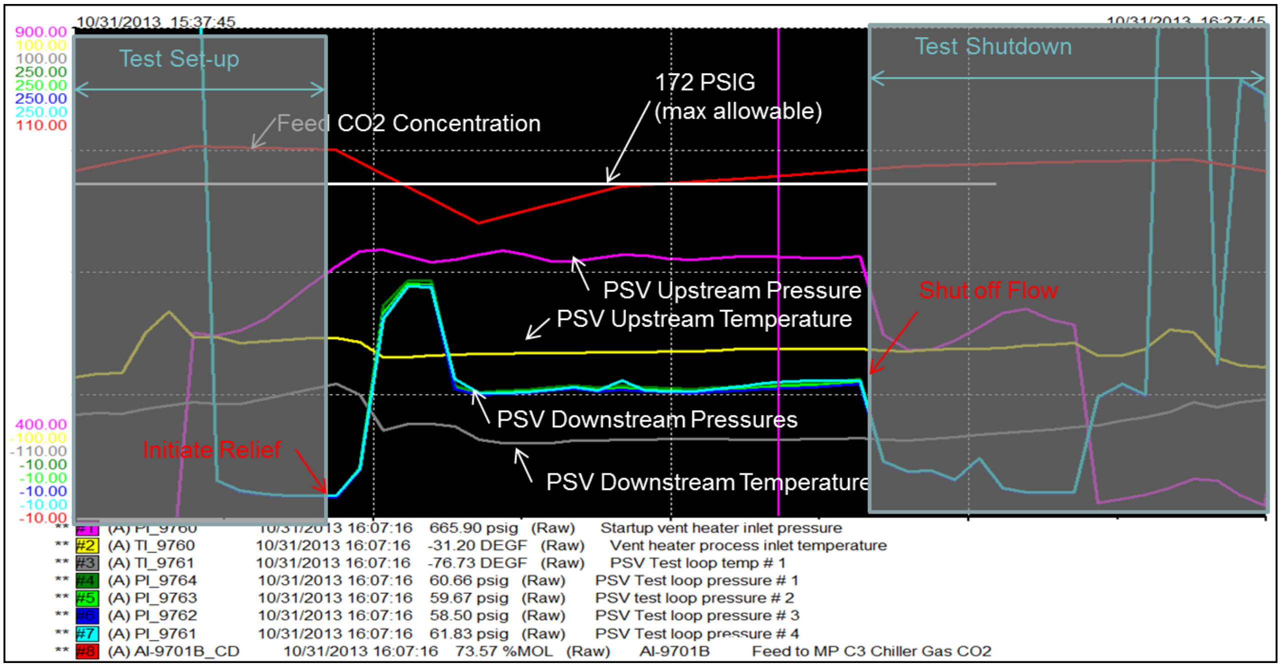
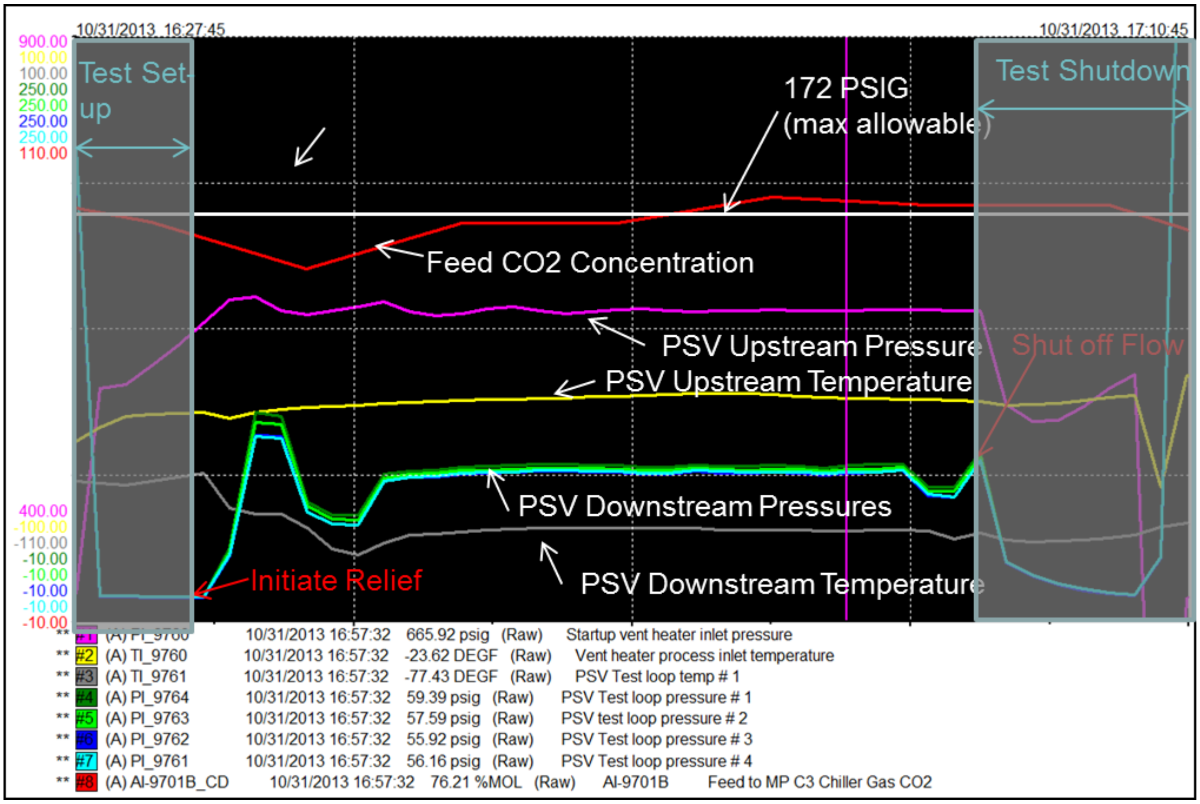


Figure 15. Liquid Relief Test A



```
** #1 (A) PI_9760     10/31/2013 16:07:16  665.90 psig  (Raw)   Startup vent heater inlet pressure
** #2 (A) TI_9760     10/31/2013 16:07:16  -31.20 DEGF  (Raw)    Vent heater process inlet temperature
** #3 (A) TI_9761     10/31/2013 16:07:16  -76.73 DEGF  (Raw)    PSV Test loop temp # 1
** #4 (A) PI_9764     10/31/2013 16:07:16  60.66 psig  (Raw)    PSV Test loop pressure # 1
** #5 (A) PI_9763     10/31/2013 16:07:16  59.67 psig  (Raw)    PSV test loop pressure # 2
** #6 (A) PI_9762     10/31/2013 16:07:16  58.50 psig  (Raw)    PSV Test loop pressure # 3
** #7 (A) PI_9761     10/31/2013 16:07:16  61.83 psig  (Raw)    PSV Test loop pressure # 4
** #8 (A) AI-9701B_CD     10/31/2013 16:07:16  73.57 %MOL  (Raw)    AI-9701B     Feed to MP C3 Chiller Gas CO2
```

Figure 16. Liquid Relief Test B



```
** #1 (A) PI_9760     10/31/2013 16:57:32  665.92 psig  (Raw)   Startup vent heater inlet pressure
** #2 (A) TI_9760     10/31/2013 16:57:32  -23.62 DEGF  (Raw)    Vent heater process inlet temperature
** #3 (A) TI_9761     10/31/2013 16:57:32  -77.43 DEGF  (Raw)    PSV Test loop temp # 1
** #4 (A) PI_9764     10/31/2013 16:57:32  59.39 psig  (Raw)    PSV Test loop pressure # 1
** #5 (A) PI_9763     10/31/2013 16:57:32  57.59 psig  (Raw)    PSV test loop pressure # 2
** #6 (A) PI_9762     10/31/2013 16:57:32  55.92 psig  (Raw)    PSV Test loop pressure # 3
** #7 (A) PI_9761     10/31/2013 16:57:32  56.16 psig  (Raw)    PSV Test loop pressure # 4
** #8 (A) AI-9701B_CD     10/31/2013 16:57:32  76.21 %MOL  (Raw)    AI-9701B     Feed to MP C3 Chiller Gas CO2
```

Figure 17. Liquid Relief Test C

After the PSV lifted, the pressure smoothly rose and steadied out around 100 psig. None of the

PSV downstream pressures approached the 172 psig threshold at any time throughout the relief. There was a visible pressure gradient, similar to the CH_4-only baseline test, across the 4 pressure transmitters in the PSV test loop. Due to the Joule Thomson cooling from depressuring across the PSV, the downstream PSV temperature reduced gradually until it steadied out around -75°F.

During these tests the feed CO_2 concentration, PSV upstream pressures, and flowrate through the PSV was difficult to keep steady. Figure 18 below highlights this issue and its impact on the downstream pressure trends.

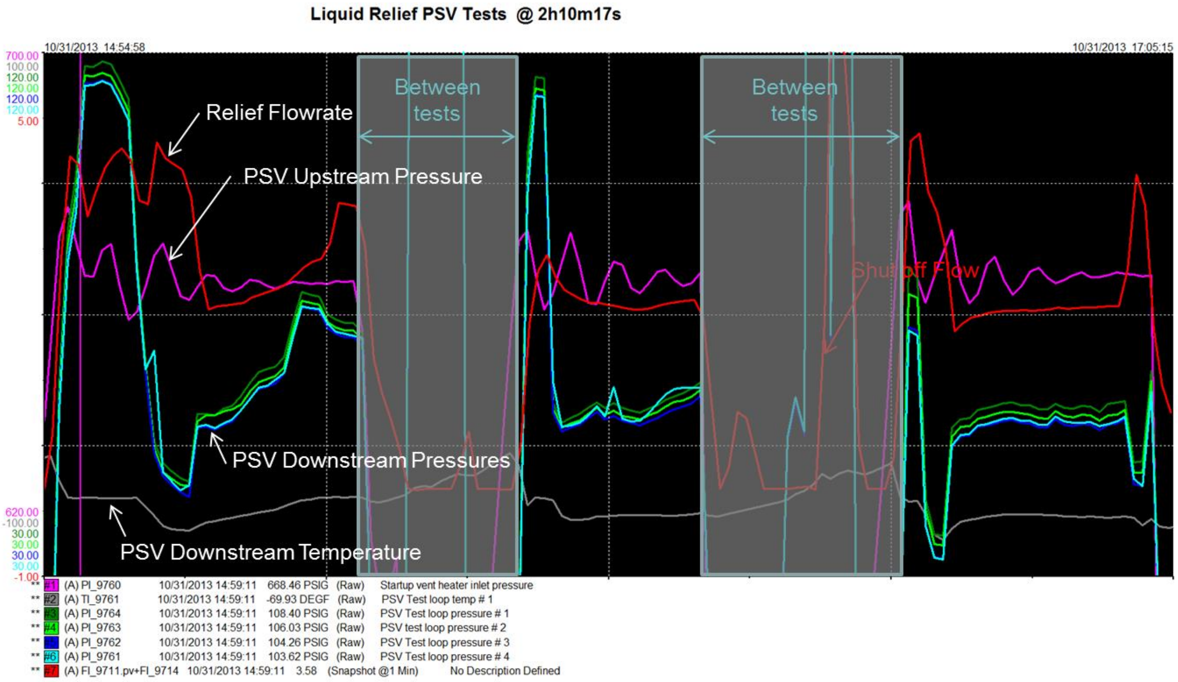


Figure 18. Liquid Relief Tests - Pressure Zoom

Figure 18 displays the PSV downstream pressures “zoomed in” so that the pressure gradient between each pressure can be seen. The relief flowrate is displayed and is intended to be interpreted as a qualitative trend instead of a quantitative value. It is possible that the vent heater was unable to melt all of the solids during the test, so the flow element measuring the downstream flowrate may not have been capturing the entire rate of the test.

One will note that in each Liquid Relief Test, the downstream pressures initially rose rapidly before falling to the steady state relief pressure. There were a couple reasons for this phenomenon. First, the fluid is relieving into a hot relief line, which initially sublimates a large fraction of the solids and causes an increased backpressure. Secondly, the operator had to control the flowrate by maintaining a constant upstream pressure. As can be seen, the pressure varied greatly at the beginning before the operator could reach a steady state. As a result, the flowrate through the PSV decreases significantly from the beginning of the relief until the steady state is reached. The downstream pressures track closely with the flowrate indicating that the variable pressures at the start of relief are a result of the changing flowrate and not solid CO_2 buildup. In Test A, there is a gradual rise in the downstream pressures, which also tracks with an increasing flowrate.

PI-9761, the last pressure measurement in the test loop, recorded a slight pressure growth during Liquid Relief Tests A and B for a brief moment, but the pressure immediately returned to match with the trends of the other transmitters. This may have indicated a brief period of solids buildup that was quickly cleared. If solid CO_2 did accumulate locally at this spot and quickly dissipated, it would support the discussion in the background that the increased force on the CO_2 accumulation was able to quickly break up the solids formation.

The system showed no indication of significant blockage in any of the piping downstream of the PSV for all three Liquid Relief Tests. The downstream pressures were relatively steady for the duration of the test and remained under the 172 psig threshold at all times. As a result, all tests met the designated acceptance criteria.

PSV Test Discussion Summary

The table below summarizes the results of all PSV relief tests. The values provided in the table are approximate average values during PSV relief.

	Data Type	Instrument	Units	Baseline	Vapor Relief A	Vapor Relief B	Liquid Relief A	Liquid Relief B	Liquid Relief C
Feed	CO2 "Inlet flow"	FE-9701C	MMSCFD	0.0	0.9	0.9	1.6	1.6	1.6
	C1 "Inlet flow"	FE-9706	MMSCFD	5.0	3.6	3.6	0.5	0.5	0.5
	CO2 mol.%	AE-9701B	MOLE %	0.0	20.0	20.0	74.6	70.6	71.3
	C1 mol.%	AE-9701B	MOLE %	97.0	79.0	79.0	25.8	29.9	29.2
	N2 mol.%	AE-9701B	MOLE %	3.0	1.0	1.0	0.6	0.7	0.7
	Feed Pressure	PI-9760	PSIG	660.0	630.0	630.0	665.0	665.6	665.1
	Feed Temperature	TI-9760	DEG F	-50.0	-56.6	-56.6	-31.1	-32.2	-23.9
Downstream of PSV	Test Loop Temperature	TI-9761	DEG F		-100.0	-100.0	-75.4	-77.0	-77.1
	Test Loop Pressure # 4	PI-9761	PSIG	100.0	105.0	105.0	62.7	58.9	56.2
	Test Loop Pressure # 3	PI-9762	PSIG	100.0	105.0	105.0	61.6	57.3	55.9
	Test Loop Pressure # 2	PI-9763	PSIG	100.0	105.0	105.0	62.9	58.2	57.4
	Test Loop Pressure # 1	PI-9764	PSIG	100.0	105.0	105.0	64.1	59.3	58.9
Simulation	Average Relief Back-Pressure	PI-9761-4	PSIG	100.0	105.0	105.0	62.8	58.4	57.1
	CO2 mol% in Relief Liquid		MOLE %	n/a	n/a	n/a	82.3	82.0	83.7
	Relief Liquid Flowrate (Estimate)		GPM	n/a	n/a	n/a	~14	~10	~10
	Gas Velocity		ft/s	202	189	189	65	46	46
	Solids Formed		WT%	0	5.4	5.4	48.55	48.51	47.27
PSV Relief Time	PSV Relief Time	-	Minutes		>12	>12	33	21	28

The PSV Tests were successfully completed for CH_4/CO_2 mixtures creating about 5 wt% solids during the Vapor Relief Tests and 48 wt% solids during the Liquid Relief Tests. The Baseline (CH_4 only) and Mixture Tests (CH_4/CO_2) gave consistent, steady results, and duplicate Mixture Tests confirmed the performance of the system. No sustained pressure excursions above the 172 psig threshold and no short-term excursions above the 225 psig threshold were observed at any time during any test.

The gas velocities in the pipe were typical flare header gas velocities for the Vapor Relief Tests. The full flow through the PSV was achieved when it popped open to 100%. A slight reduction in the velocity was seen from the methane baseline, in part because a small fraction of the stream converted into dense, solid CO_2. However, the estimated velocities dropped significantly in the Liquid Relief Tests because (A) the PSV capacity was reduced by approximately 50% and (B) a large fraction of the stream converted into solid CO_2. In addition, there was a brief period in which the modulating PSV was opening in which even lower velocities were present. It would appear that the low velocities of the Liquid Relief Tests were still able to entrain the solids at up to 48 wt% solid CO_2.

Conclusions

A commercial-scale experimental study was performed at ExxonMobil's Shute Creek Treating Facility to test the ability of relief lines to handle solidifying CO_2 particles during pressure relief at different test conditions. Two Vapor Relief Tests of 80% CH4 / 20% CO2 mixtures formed an estimated 5 wt% solids, and three Liquid Relief Tests of 20% CH4 / 80% CO2 mixtures formed an estimated 48 wt% solids. All tests met the following pre-determined success criteria:

1. No full blockage of test piping downstream of PSV is observed within 10 minutes of relief.
2. Downstream pressure does not exceed 75% of design pressure (172 psig) for ANSI 150# stainless steel flanges at cryogenic temperatures, over a sustained period.
3. Short term pressure excursions do not exceed 100% of design pressure (225 psig) for ANSI 150# stainless steel flanges at cryogenic temperatures.

Two types of pilots, modulating and non-modulating, were tested on a 1"x2" PSV which relieved into a "tortuous path" of piping with four (4) 90° elbows and a 2"x4" expansion and contraction in the piping at the smallest PSV outlet diameter allowed per API 526. The test met all the criteria for a successful PSV relief test and demonstrated CO_2 containing fluids generating approximately up to 48% by weight solids can be relieved without obstructing the relief piping.

Most significantly, there were no signs of significant solids blocking in the relief piping despite relief into a "tortuous path" of piping at low velocities, generating significant amount of solids over a long period of time.

References

1. ExxonMobil Corporation, 2015. The Outlook for Energy: A View to 2040.