ADDENDUM TO THE FINAL REPORT ON:

TESTING AND ANALYSIS OF THE PERFORMANCE OF PRESSURE RELIEF VALVES FOR CUSTOMER TANKS

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Notice

Acknowledgments

The authors wish to express their appreciation to the individuals and organizations who contributed to the successful completion of this challenging program. The authors sincerely appreciate the support in time, materials, and shipping expenses for those propane marketers and National Propane Gas Association members that supplied pressure relief valves for this testing program and the efforts of the Propane Education & Research Council (PERC) and National Propane Gas Association (NPGA) to assist with the collection of the pressure relief valve samples for testing. In addition, we would also like to thank the pressure relief valve manufacturers and industry experts that provided feedback on the test protocol. This project would not have been a success without their assistance.

The authors also wish to acknowledge the program advice and guidance provided by Larry Osgood of Consulting Solutions on behalf of PERC. Larry imparted into the program the practical propane industry experience very necessary in this type of project.

EXECUTIVE SUMMARY

In 2009, Battelle completed an experimental test program of nearly 400 pressure relief valves (PRVs) that had been removed from service to attempt to determine if the 10 to 15 year recommended service life for PRVs from several manufacturers could safely be extended. This program considered information gathered from manufacturers and from tests performed on nearly 400 PRVs removed from service, varying in age from less than one year to more than sixty years. The sample of PRVs was tested to a protocol that was developed from selected test procedures contained within Underwriters Laboratory standard (UL) 132, *Safety Relief Valves for Anhydrous Ammonia and LP-Gas*.

UL 132 is intended to establish the initial operating parameters of newly-manufactured PRVs, as well as other performance specifications. The test procedures adapted for use for this test program were based primarily on Section 11, start-to-discharge/resealing pressures of safety valves. According to UL 132, an acceptable start-to-discharge pressure range is 100 to 110 percent of the set pressure while an acceptable resealing pressure range is greater than 90 percent of the set pressure. These values were used as part of the criteria to determine the variance in PRV performance, however additional criteria were also selected to reflect the fact that PRVs should achieve full flow by 120 percent of the set pressure and the PRV blow-down pressure is acceptable down to 65 percent of the set pressure according to UL 132.

The findings from this experimental program found that:

- PRVs start showing signs of inconsistent performance against the UL 132 criteria for new valves shortly after installation. The initial start-to-discharge pressures ranged from 50 psig below the PRV set pressure to 100 psig above the maximum set pressure per UL 132 (275 psig for 250-psi set point valves).
- As the PRV ages, the tendency for inconsistent performance increases (25 to 60 percent probability that a PRV 60 years of age will stick closed; 40 to 80 percent probability that valves older than 40 years of age will have a high start-to-discharge pressure).
- Once a PRV has discharged, its performance often becomes unreliable if required to immediately discharge again (50 to 75 percent probability that new valves will open below their set pressure in start-to-discharge trials conducted minutes after the first trial).
- Other factors (environmental conditions, manufacturer, PRV type, and PRV size) were evaluated but not found to correlate with PRV performance issues.

Battelle, working with the Propane Education & Research Council (PERC) Retail Operations Task Force and Research & Development Advisory Committee (RDAC), had identified three additional tasks to provide data on how PRVs might perform under more ‘real world’ test conditions and to better understand the contributing factors to PRV performance. These three tasks are as follows:

- Task A1 – Performance of PRVs under ‘real world’ conditions. This task included a literature review and basic thermal modeling to determine real world conditions that require a PRV to operate. It also included testing of some PRVs under similar conditions and an assessment of the elastomeric material performance at elevated temperatures.

- Task A2 – Survey members of the propane industry and conduct literature and web searches to identify claims of specific issues with PRV field performance. This task compiled information on reported PRV incidents in the field.
- Task A3 – Functional design review and additional failure analysis of test PRVs. This task included detailed examinations of tested PRVs with low start-to-discharge pressures, high start-to-discharge pressures, and PRVs that did not open.

Task A1 – Performance of PRVs under 'real world' conditions

The main performance issues that were evaluated in the original test program included:

- PRV did not relieve by 375 psi
- PRV start-to-discharge pressure below the set pressure
- PRV start-to-discharge pressure higher than 120 percent of the set pressure
- PRV resealing pressure lower than 90 percent of the set pressure

The maximum test pressure was limited to 375 psi primarily for safety reasons and it also represents the hydrotest pressure for ASME tanks with a working pressure of 250 psi. The criteria specifying a start-to-discharge pressure higher than 120 percent of the set pressure was selected as this represents the pressure at which a new PRV should be fully open according to UL 132. The two additional criteria (start-to-discharge lower than the set pressure and resealing pressure lower than 90 percent of the set pressure) were chosen since they represent potential chronic leak and safety issues for a PRV.

This new test program evaluated a narrow data set of 14 PRVs under various more 'real world' conditions, including elevated temperatures (130°F), slow pressure rise rate (0.004 psi/s), and/or propane conditioning prior to testing. Three sets of tests were conducted 1) a sample of four previously untested PRVs and two previously tested PRVs that were found to be 'stuck' shut at 0.004 psi/s and 130°F; 2) a sample of two previously untested PRVs and one previously tested PRV that was found to be 'stuck' shut with propane conditioning of the valves; 3) a sample of five previously tested PRVs that were found to be 'stuck' shut at 0.004 psi/s, 130°F, and propane conditioning.

Test Set 1: Slow Pressure Rise and Applied Heat: Six 250-psig set point PRVs were tested using a slow pressure rise rate and external heating. The test matrix was comprised of two newer untested PRVs (<20 yrs old), two older untested PRVs (>20 yrs old), and two previously tested PRVs that were found to be stuck shut. As shown in Table ES-1 all PRVs tested under these conditions opened, including those that were previously found to be 'stuck' shut. Three of the PRVs, all at least 30 years old, exhibited high start-to-discharge behavior with opening pressures higher than 275 psig (the UL 132 start-to-discharge criteria for new 250-psig set pressure PRVs).

Table ES-1 - Results of New Test Procedure (Slow Pressure Rise and Applied Heat)

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Opening Type
475	Internal	3/4"	9	No	246	Slow open
49	Internal	3/4"	17	No	252	Slow open
208	Internal	3/4"	28	No	271	Popped
394	Internal	3/4"	30	No	327	Popped
326	Internal	3/4"	45	Yes, Stuck	355	Popped
274	Internal	3/4"	43	Yes, Stuck	328	Popped

Test Set 2: Propane Conditioning (original test protocol): Another three 250-psig set point PRVs were conditioned in a propane environment and tested using the original test procedure (increasing pressure at 0.5 psi/s, no external heating of the PRV, and the visual observation of bubbling as indication that the PRV opened). Like the original test program, the test procedure was repeated three times in close succession for each PRV. The test results are summarized in Table ES-2. All three PRVs opened under this test procedure. Two of the PRVs still had high start-to-discharge pressures; both of which were greater than 20 years old (one was determined to be 'stuck' closed in the previous test program).

Table ES-2 - Results of Original Test Procedure with Propane Conditioning of PRVs

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Reseat Pressure (PSIG)
484	Internal	1"	10	No	264	264
					267	266
					268	267
407	Internal	1"	32	No	329 (Popped)	---
					287	260
					287	259
350	Internal	1"	22	Yes, Stuck	352	314
					327	311
					323	308

Test Set 3: Slow Pressure Rise, Applied Heat, and Propane Conditioning: To obtain more confidence in the test results, an additional five 250-psig set point PRVs were tested. All five of these PRVs had been tested in the original test program and found to be stuck shut. The five PRVs were conditioned in propane for at least four days prior to testing and then subjected to the test procedure with a slow pressure rise and external heating. The intent of the additional testing was to increase confidence that the new more 'real world' test conditions consistently resulted in improved PRV performance.

The test results are summarized in Table ES-3. Four of the five previously tested and 'stuck' shut PRVs opened under the new test conditions and all four exhibited high start-to-discharge pressures (> 275 psig). One PRV remained stuck shut after reaching the test limit of 375 psig. This valve was further pressurized to 500 psig without opening (at this pressure the test was terminated for safety concerns). All PRVs tested in this group were greater than 40 years of age.

PRV 62, which did not open under the new test conditions, was subsequently examined in the failure analysis task (Task A3). During that examination, severe corrosion was found such that the spring was chemically bonded to the valve body and a load of 832 pounds was required to free the spring and sleeve from the valve body. It should be noted that PRV 62 is an external type valve which are no longer installed on new tanks.

Table ES-3 - Results of New Test Procedure (Slow Pressure Rise and Applied Heat) on Additional Stuck Valves with Propane Conditioning

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Opening Type
175	External	3/4"	40	Yes, Stuck	345	Popped
173	Internal	3/4"	44	Yes, Stuck	347	Slow open
102	Internal	1”	52	Yes, Stuck	308	Slow open
62	External	3/4"	57	Yes, Stuck	Did not open	
10	Internal	1”	58	Yes, Stuck	285	Slow open

Figure ES-1 compares the initial start-to-discharge pressures to the performance criteria and age for the 250-psig set point PRVs tested in this program. The vertical axis is the parameter tested (pressure) while the horizontal axis is an indication of the age of the PRV tested. The colored horizontal lines represent the start-to-discharge, full open, resealing, and blow-down pressure limits as specified in UL 132. The different data symbols represent the test variables used for that particular valve (O = conditioned, 0.5 psi/s, not previously tested; Δ = not conditioned, 0.004 psi/s, stuck PRV; X = not conditioned, 0.004 psi/s, not previously tested; □ = conditioned, 0.004 psi/s, stuck PRV; + = conditioned, 0.5 psi/s, stuck PRV). The darker gray band represents the range of acceptable PRV performance per UL 132. Data points that are circled with the label ‘DNO’ signify PRVs that did not open by 375 psi. Significant differences between ages are evident by the variation in the vertical spread of the data points.

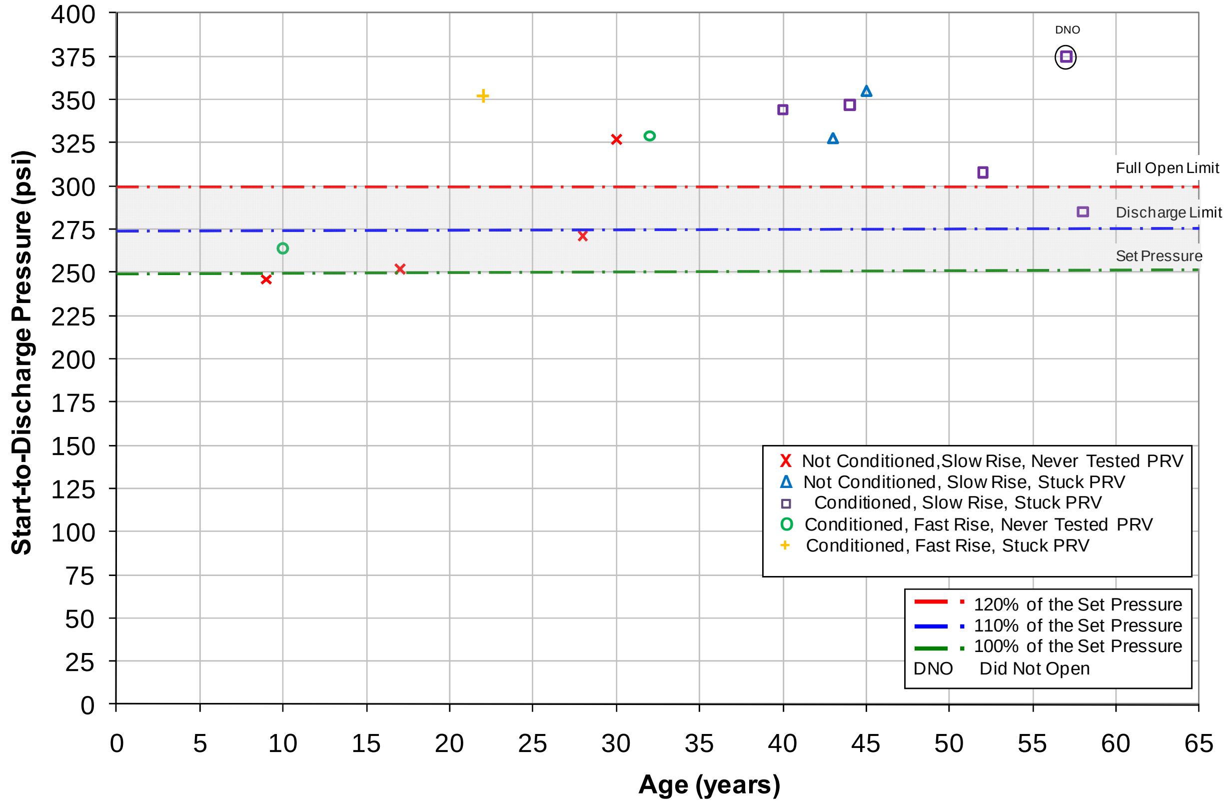

Figure ES-1 - Results of All Additional Testing for 250-psig Set Point PRVs

The results for the new test conditions show that PRVs less than 20 years old generally performed within the UL 132 criteria for new valves (with one opening 2 psi lower than its set pressure). One 22 year old PRV had high start-to-discharge and resealing pressures. When this valve was examined, it was found to have the highest spring load and load-displacement value of all PRVs with comparably sized springs. The high spring load caused by a higher load-displacement value and a greater installed displacement may indicate that the PRV factory set pressure was set high. All PRVs 30 years old and greater opened at high start-to-discharge pressures (>275 psig).

Of the eight previously stuck PRVs tested, seven opened under the new test conditions indicating that propane conditioning, heating, and/or low pressure rise rates have an influence on the performance of PRVs removed from the field. All seven of the previously 'stuck' closed PRVs that opened under the new test conditions still exhibited high start-to-discharge pressures (in excess of 110 percent of the set pressure) but opened within 1.5 times the set pressure (hydrotest pressure for ASME tanks with a working pressure of 250 psi). Additional analyses of PRV 62 (external type valve no longer installed on new tanks) indicated severe corrosion caused it to remain stuck under the new test conditions.

The new experimental test results indicate that 'real world' conditions make a difference in how the PRVs perform for this limited data set and they still show a deterioration in performance (per UL 132 criteria) based on the age of the PRV which increases for valves 30 years old and older.

Task A2 – Propane Industry Survey to Document PRV Incidents in the Field

Fifteen members of the propane industry representing a cross section of PRV manufacturers, tank manufacturers, researchers, and those involved with propane industry programs (e.g. PERC Safety & Training) were contacted by Battelle. The type of data requested from these sources included ASME tank failures, especially if there was documentation that the PRV was noted to be (or not to be) functioning, and other documented PRV incidents for various sizes of valves (i.e. ASME tanks, cylinders, transports). This information was supplemented with limited web searches and literature for the same type of data.

Based on the information collected, Battelle was able to document six PRV related incidents. Three documented incidents were due to a PRV being stuck shut (blockages from ice or debris); two incidents were due to PRV exposure to off-specification product high in H_2S in which the valve spring cracked and failed; one incident was from an unknown cause in which the PRV on a propane vessel failed in the closed position during a fire test of the vessel. The root causes for five of the six incidents were attributed to external factors (off-specification product or valve blockages), not the manufacture or age-related deterioration of the PRV. The cause of the sixth incident was unknown and the report documenting this incident was unavailable for review.

Three incidents were reported in the literature in which storage tanks ranging in size from 1,000 gallons up to 18,000 gallons BLEVE'd in a fire. All three incidents reported that the PRVs had relieved per their intended design.

There were also three incidents reported where a PRV discharged while someone was looking over the PRV causing them injury. These last three incidents were not included as part of the PRV incident data as there was not enough information to discern if the tank was overfilled causing the PRV to relieve per its design or if there was another issue with the PRV.

Considering there are over 12 million propane tanks currently in use and a maximum of six incidents that could be documented from this review (five of which were attributed to external factors), the known incident rate for PRVs in the field is low.

Task A3 – Functional design review and additional failure analysis of test PRVs

Battelle conducted a failure analysis of select PRVs that did not meet the performance requirements (per UL 132, Section 11 criteria for newly-manufactured valves) from the original test program to determine possible mechanisms and variables that may have contributed to the observed behavior. The examinations included observations of the conditions of the valves (visually and under a low power stereomicroscope), infrared analyses on the sealing gaskets to identify the materials from which they are made, Shore D hardness measurements on the gasket materials, and forensic analyses of the valves once disassembled. As the valves were being disassembled, the spring force versus deflection was measured and the spring characteristics were analyzed to determine whether changes, such as stress relaxation, occurred during service or whether the spring characteristics for PRVs from a given vendor are consistent.

These examinations and measurements were made on 12 valves that were 'stuck' closed (did not open by 375 psig) in the original test program, 16 valves that exhibited high start-to-discharge pressures (greater than 110 percent of the set pressure), and 10 valves that exhibited low start-to-discharge pressures (less than the set pressure). In addition, six valves that were not tested during the previous study but were tested in the present study were visually examined and one was disassembled for more detailed examinations (PRV 407). A new valve (PRV 146) from Manufacturer A was also disassembled and examined to provide data for comparison of the spring force measurements and the gasket materials with the PRVs that had been removed from service.

Some of the valves that were disassembled in the initial performance testing program were also reexamined to see if additional data on the cause of their observed behavior could be determined. These valves consisted of four that were 'stuck' shut, five with high start-to-discharge pressures, and four with low start-to-discharge pressures. The results for all valves examined are summarized below.

Spring Analyses: The spring characteristics from the disassembled PRVs were evaluated to determine if there were common spring sizes and strengths (load-displacement characteristics), particularly for those springs used by specific PRV manufacturers.

Comparison of the data showed there was no correlation between the PRV performance (did not open, high start-to-discharge or low start-to-discharge) and the load-displacement value or the PRV spring load. Although new springs of each size were not available to compare the load-displacement characteristics to assess possible stress relaxation, the calculated PRV spring loads were plotted versus the age of the PRVs as shown in Figure ES-2. The numbers next to the symbols in the chart represent the PRV identification number.

Figure ES-2 does not indicate a loss in PRV spring load as a function of time in service. Thus the spring analyses from the various PRVs evaluated does not indicate that stress relaxation (load loss) contributed to the deterioration in PRV performance. Figure ES-2 does indicate that spring loads for the PRVs that were less than 20 years old ranged between about 130 and 145 pounds; whereas for the PRVs that were greater than 20 years old, the spring loads had greater variation between 125 and 227 pounds. In addition, all of the PRVs that did not open during the initial test program had spring loads of 150 pounds or greater. Unfortunately, many variables related to the valve and spring sizes will influence the spring load and those variables may account for the greater scatter in the older PRVs. Since the manufacturing specifications for the springs and the PRVs produced at different times were not available for review, it cannot be concluded that the differences observed reflect changes in design requirements or spring manufacturing procedures.

As shown in Figure ES-2, there was one PRV (PRV 350) that had a higher spring load, 227 pounds, than the others. That spring also exhibited the highest load-displacement value and had the largest installed spring displacement for the group of comparably sized springs. Calculations of the spring load and exposed gasket area indicate a pressure of approximately 315 psig would be required to open the valve (overcome the spring load). Thus, the high spring load for PRV 350 was caused by a spring with a higher load-displacement value and a greater installed displacement, i.e. the PRV factory set pressure likely was set high.

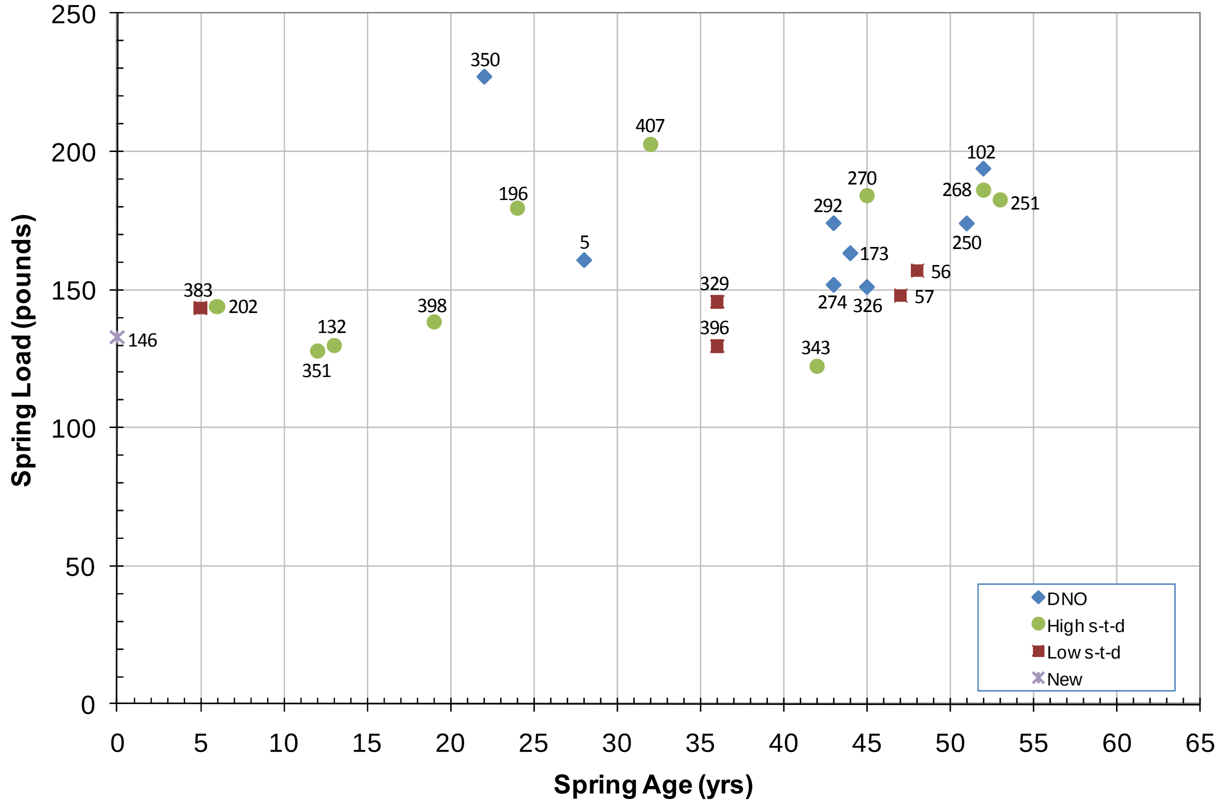

Figure ES-2 – PRV Spring Load versus Age

Seat Disc (Gasket) Material Analyses: Gaskets from the PRVs selected were examined to 1) assess their overall appearance after being in service, 2) determine the rubber or polymer material from which the gaskets were made, and 3) measure the hardness of the gasket material. In addition, if the gasket stuck to the valve body when the PRV was disassembled, the load required to break the seal was measured by pushing on the valve stem in an Instron universal testing machine.

When the 38 PRVs were disassembled for detailed examinations, the gasket stuck to the valve body in five of the PRVs. Those PRVs and the loads and displacements required to break the seal are listed in Table ES-4.

As shown in Table ES-4, the loads required to loosen the gaskets from the valve bodies ranged from about 20 to 136 pounds and the displacements ranged from 0.005 to 0.023 inch. The measured displacements show that these gaskets exhibited some elasticity. Considering the area of the gasket and the load to dislodge the gasket, the equivalent estimated start-to-discharge pressures for these PRVs are estimated to be 208 psi or lower. Consequently, if the gasket was the only factor contributing to the PRV performance issues, the test pressures used in the initial study should have dislodged the gaskets. As such, the data indicate stuck gaskets may contribute to but are not the main cause of the failure of the PRVs to open at their set pressures. However, it has been suggested that the spring force and the gasket-stuck force may be additive. In other words they are similar to two springs in series. Experiments would need to be designed and conducted to resolve this issue and is outside the scope of this analysis.

Table ES-4 – Loads and Displacements to Dislodge Gaskets from the Valve Bodies after PRV Disassembly

PRV ID	PRV Set Pressure (pisg)	Load (lbs)	Displacement (in)[1]
173	250	20.1	0.022
274	250	56.9	0.016
5	275	31.6	0.011
250	250	115.6	0.023
292	250	135.9	0.005

FT-IR analyses indicated that the gaskets in all but two of the PRVs were made from Buna N or modified Buna N. In some cases, a filler material was also identified. The gaskets from the other two PRVs examined were made from Viton.

The hardness of the gaskets ranged from 17 to 58 Shore D. However, the original hardness of the gaskets when produced was not known; thus estimates of how gasket hardness may have changed over time could not be made. The hardness of all the gaskets by performance issue (did not open, high start-to-discharge, low start-to-discharge) was plotted versus their age to see if there were general trends in their behavior over time (see Figure ES-3). The data shows no strong trends or correlations.

All of the gaskets exhibited compression set rings, as would be expected. The compression set rings were somewhat off-center on the gaskets from PRVs 350 (did not open), 281 (high s-t-d), 7 (did not open), and 5 (did not open). As indicated, three of these PRVs did not open in the original test program and one exhibited a high start-to-discharge pressure. It is possible that this condition indicates misalignment of the valve stem/poppet in the PRV which could have contributed to their performance issues during testing. Misalignment of the valve stem could result in a strong interaction between the valve stem surface and the guide spacer inner surface which could increase the load required to open the valve. Also moisture condensation in those regions could promote crevice corrosion which again could contribute to higher valve opening loads.

The other features that indicate some deterioration of the gaskets during service were regions of material breaking off the outer edge of the gasket, radial and circumferential cracks in the outer circumferential ring (beyond the gasket seal region), roughened 'alligator skin' surface features, fragmenting of the gasket during removal, and finally regions of pull out from the seal surfaces and gasket material transfer to the valve body seal surfaces. Except for the latter conditions, the deterioration was located beyond the seal area region and should not have had an effect on the performance of the PRVs. The material pull out and material transfer issue may contribute toward sticking but the equivalent pressures to overcome that condition were less than the PRV

[1] The values in the displacement column represent the distance on the X-axis of the load displacement curve before the load dropped indicating that the gasket was free. The gaskets showed some elastic behavior before they broke loose.

set pressures and obviously less than the maximum test pressure of 375 psig. The only condition identified during the examination of the gasket material that conclusively resulted in the recorded PRV performance was the broken gasket in PRV 211 (discharged immediately when tested).

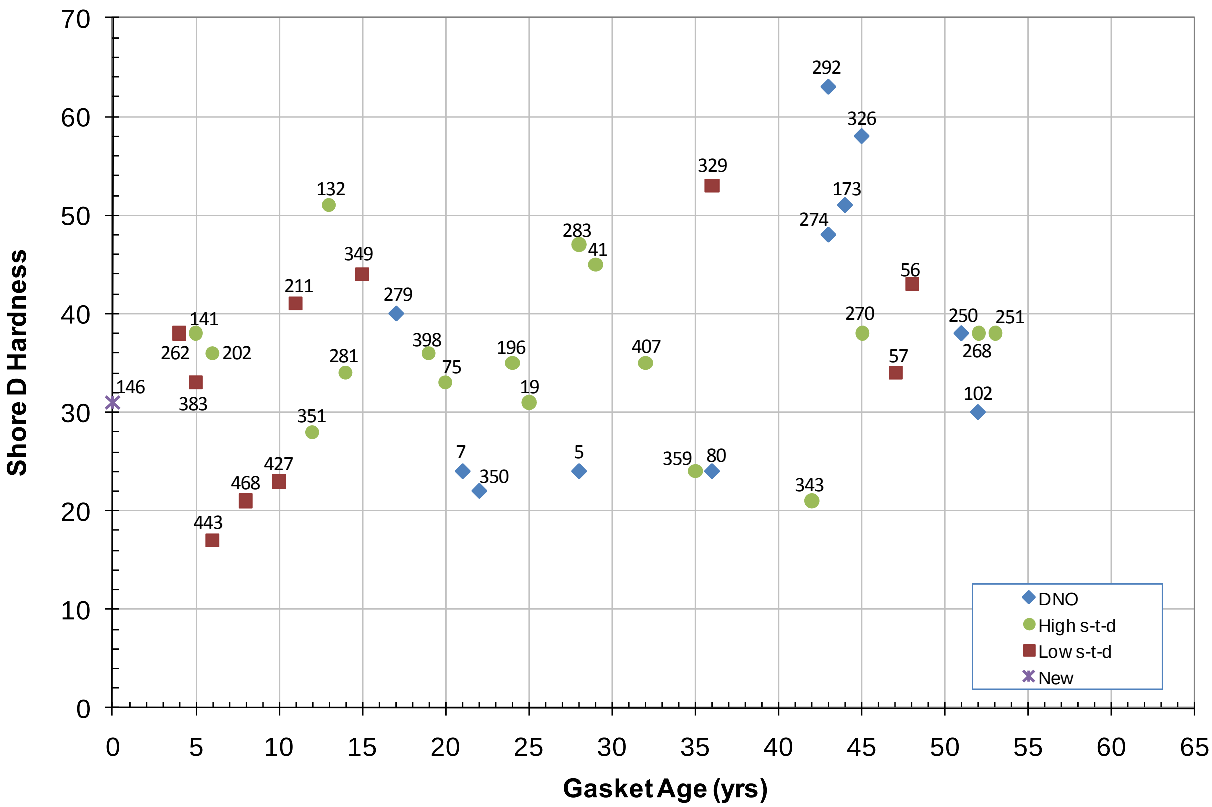

Figure ES-3 – Gasket Hardness versus Age

Rain Cap Analyses: When the pressure relief valves selected for examination were examined visually, it was observed that only 10 of 43 valves had rain caps included with the valve. The PRVs were further examined for evidence of either an external or internal rain cap line that would indicate if a rain cap had been present and possibly just not included with the valve when shipped for the performance testing program. This analysis showed that about 60-percent (25 of 43) of the PRVs that were studied had evidence of a rain cap being present even though one may not have been included with the valve provided for study. For the 40-percent of PRVs without evidence of a rain cap being present, eight of these PRVs did not open in the original test program and only one met the UL 132 start-to-discharge performance criteria for new valves. The Battelle investigators strongly suggest that more attention to the presence of rain caps be given by tank users and tank service personnel. Keeping a rain cap in place should minimize debris from entering the valve.

Summary of Findings:

PRVs that Did Not Open: The analysis of the PRVs that did not open by the test pressure of 375 psig in the initial performance testing program revealed a number of conditions that may have contributed to this behavior. These conditions include

- Corrosion,
- Interaction between the valve stem and the guide spacers (perhaps resulting from misalignment), and
- Sticking of the gasket to the valve body.

However, for only one of the PRVs (PRV 62) was there conclusive evidence for the demonstrated behavior. In PRV 62, which is an external type PRV, the spring and sleeve were severely corroded and the corrosion products essentially 'locked' the spring and sleeve within the valve body. As discussed previously, PRV 350 had a high spring load and a greater installed displacement indicating the PRV factory set pressure was set high. PRV 350 also showed signs of mild corrosion, a stuck gasket, and possible misalignment. For the other PRVs examined, a combination of two or more of the conditions mentioned previously may have contributed to the 'sticking' closed behavior of the valve; however none of the evidence was conclusive.

PRVs that Exhibited High Start-to-Discharge Pressure Behavior: Twelve PRVs that exhibited high start-to-discharge pressures were examined to determine conditions that would conclusively explain the behavior. Most of these PRVs initially discharged at a high start-to-discharge pressure but opened in subsequent trials near or below the set pressure. The examinations revealed several conditions that may have contributed to the high start-to-discharge pressure. These conditions include

- Corrosion,
- Interaction between the valve stem and the guide spacers,
- Possible valve stem misalignment, and
- Sticking of the gasket to the valve body.

However, the evidence was conclusive for only one of these PRVs (PRV 398). PRV 398 had a zinc coated spring and valve stem with significant amounts of zinc corrosion products on the valve stem and guide spacer that likely resulted in the high start-to-discharge pressure behavior. PRV 41 exhibited a strong interaction zone between the valve stem and the guide spacer that could have caused the valve to exhibit high start-to-discharge behavior.

The high start-to-discharge behavior followed by more normal opening and sealing behavior is not unexpected for devices that have different materials in contact under static loads for extended periods of time even if extensive corrosion or material transfer has not occurred.

PRVs that Exhibited Low Start-to-Discharge Pressure Behavior: Eleven PRVs that exhibited low start-to-discharge pressures were examined and for only one of the eleven PRVs examined was there conclusive evidence for the demonstrated behavior. That valve was PRV 211 which had a broken gasket and leaked immediately when pressurized. However, the cause of the broken gasket under service conditions could not be determined from the evidence obtained in this study.

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Terms and Acronyms

ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BPVC	Boiler and Pressure Vessel Code
BLEVE	Boiling Liquid Expanding Vapor Explosion
BTU	British thermal units
CGA	Compressed Gas Association
DOT	United States Department of Transportation
FT-IR	Fourier Transform-Infrared
gal	gallons
hr	hour
lbs	pounds
LPG	Liquefied petroleum gas
MAWP	maximum allowable working pressure
NPGA	National Propane Gas Association
PERC	Propane Education & Research Council
PRD	pressure relief device
PRV	pressure relief valve
psi	pound per square inch
RDAC	Research & Development Advisory Committee
s	second
s-t-d	start-to-discharge
UL	Underwriters Laboratories

1.0 OVERVIEW

In 2009, Battelle completed an experimental test program of nearly 400 pressure relief valves (PRVs) that had been removed from service to attempt to determine if the 10 to 15 year recommended service life for PRVs from several manufacturers could safely be extended. This program considered information gathered from manufacturers and from tests performed on nearly 400 PRVs removed from service, varying in age from less than one year to more than sixty years. The sample of PRVs was tested to a protocol that was developed from selected test procedures contained within Underwriters Laboratory standard (UL) 132, *Safety Relief Valves for Anhydrous Ammonia and LP-Gas*.

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This report summarizes the findings from these additional tasks as an addendum to the original final report submitted in April, 2011 [19].

2.0 PERFORMANCE OF PRVS UNDER REAL WORLD CONDITIONS (TASK A1)

One of the issues identified after completion of the original test program is that the laboratory conditions did not accurately mimic 'real world' operating conditions. Specifically, the PRVs tested in the original program had been removed from propane service for a period of six months or longer which is not representative of actual PRV operating conditions on a propane tank. In addition, the PRVs were tested at room temperature. However, for many field installations the PRV will experience radiant heating effects and may be at a higher temperature if called on to function. Also in respect to 'real world' conditions, a PRV could also be at a lower temperature and still relieve if the tank experiences an extreme overfill condition. For these reasons, a test program that considered PRV performance under a range of actual operating conditions was recommended.

A second issue with the original test program is that it was designed using Underwriters Laboratory standard (UL) 132, *Safety Relief Valves for Anhydrous Ammonia and LP-Gas*. Although this standard works well for new valves, it is not designed to represent conditions experienced by valves in the field. In particular, for the start-to-discharge/resealing pressure testing, the pressure rise rate is listed at no greater than 2 psi/s once the pressure to the valve is within 25 psi of the marked set pressure. For the Battelle test program, we chose a pressure rise rate of 0.5 psi/s once the pressure to the valve was within 35 psi of the marked set pressure. The rate was chosen to minimize the time required for each test while still maintaining a margin such that the pressure rise rate did not exceed the limit in UL 132. However, when considering the 'real world' pressure rise rate within a propane tank, it is likely far less than even 0.5 psi/s, even on the warmest of days.

As such, this task was designed to better understand what the 'real world' conditions might look like and to use these 'real world' conditions to test several PRVs to determine if the results differ from the original test program. The activities envisioned for this task included:

1. Conduct a literature review of propane tank temperature/pressure relative to ambient weather and fire conditions; identify any research on the temperature of specific tank components (PRVs) relative to ambient weather conditions and fire conditions. Estimate the temperature of PRVs and tanks under various ambient conditions (hot environment and fire) through calculations and/or literature review.
2. Identify common elastomeric materials used in PRV construction (e.g. seat disc). Compile information regarding the performance of these materials as a function of temperature. Evaluate the possible impact on valve performance based on the estimated temperatures of PRVs and the material properties.
3. Conduct thermal modeling of 500 gallon and 1,000 gallon steel propane tanks with paint coating to determine pressure rise rate in tank. Investigate different fill levels and an average daytime/nighttime summer temperature in Arizona.
4. Conduct additional testing of previously untested PRVs and 'stuck' PRVs to see if results differ from original tests. One series of tests was designed to replicate the conditions of

an overfilled tank subjected to ambient weather heating: slow pressure rise rate and slightly elevated PRV temperature. Another series of tests considered the effect of 'conditioning' the PRV in propane for several days at normal tank pressures before executing the PRV relief test. The 'conditioning' tests evaluated PRVs under the original test program conditions and 'stuck' PRVs under the new testing conditions (slow pressure rise rate and elevated temperatures).

5. Review propane tank design requirements and compare to the design requirements of other comparable pressure vessels.

2.1 Literature Review of Propane Tank Ambient Temperature and Pressure Conditions

A literature review was conducted to identify what has been reported about real world temperature and pressure conditions to which PRVs are exposed. The objective was to identify the maximum pressures expected to be encountered in various scenarios and the associated rate of pressure change to reach those pressures.

The literature review was conducted using keyword searches on the EiCompendex database of journal, conference, and trade publications. The keywords used included subsets, derivations, and combinations of the following terms:

- Propane, LPG
- Temperature, thermal
- Pressure
- Cycle, cyclic, daily, diurnal
- Solar, solar heating, radiation, radiative
- Tank, vessel
- PRV, relief valve, overpressure, overfill

After articles were acquired and reviewed, the literature review was expanded to include relevant documents cited by articles identified in the keyword search.

A majority of the articles reviewed focused on propane tank response in fire conditions. These articles covered both experimental testing and numerical simulation of fire events. Few articles were found that dealt with subjects such as ambient heating of propane tanks, the behavior of PRVs under ambient heating conditions, or PRV response to overfilling. However, the insight gained from these articles is sufficient to give a general idea of more 'real world' conditions that PRVs encounter.

The results summarized below focus on the particular aspects of the literature review relevant to addressing the fundamental tank performance issues; the maximum tank pressure and associated rate of pressure change seen in a propane tank.

2.1.1 Ambient Heating of Propane Tanks

A single article was found that concerned the heating of propane tanks by ambient weather and solar radiation. [1] A lumped parameter model of a propane tank was created and used to predict propane behavior when subjected to daily weather conditions. The model assumes a uniform saturated mixture of propane at the tank temperature and no stratification of liquid temperatures and resulting differences between the vapor pressure and liquid pressure. This assumption is required to create a thermal model that can be solved within the time and budget constraints of the task. While thermal stratification exists to some degree in every propane vessel subjected to a transient change in thermal loads, the effects of stratification are much more significant under very high thermal loads, like fire, and much less significant for lower thermal loads, like ambient weather conditions. The net effect of thermal stratification is that the PRV will realize a faster rate of pressure rise than would be predicted by a model that assumes a uniform mixture. Therefore the rates predicted by a model that assumes a uniform mixture should be considered the lower limit of pressure rise rates seen by the PRV. The model predicts a combined solar and ambient heat flux on the order of 10 W/m^2.

The model presented in the article was validated with experimental data. The experimental testing was carried out on a small DOT cylinder (4 lb), a medium DOT cylinder (13 lb), a large DOT cylinder (100 lb) and a 30,000 gallon ASME tank. All of the scenarios gave reasonable validation to the lumped parameter model, even when measurements indicated there was some thermal stratification inside the test vessel. It should be noted that substantial changes in tank temperature and pressure were predicted for the DOT cylinders (small thermal mass) and very little change for the 30,000 gallon ASME tank (large thermal mass). The focus of this investigation is on 500 and 1,000 gallon tanks which fall somewhere between the two extremes in size that were considered in this article.

For the two smallest containers subjected to ambient weather heating, a change in temperature of about 21°F was recorded over a period of 5 hours during the day. Assuming saturated propane (a close surrogate for typical propane mixtures) at the recorded temperatures and a linear change in pressure, the rate of pressure change for ambient heating only is approximately 8 psi/hr (0.002 psi/s). When those same cylinders were placed in direct sunlight, in addition to the ambient weather heating, the change in temperature was measured to be 53°F over 5 hours. Again assuming saturated propane at the recorded temperatures and a linear change in pressure, the rate of pressure change for ambient and solar heating is 22 psi/hr (0.006 psi/s).

By our judgment, this thermal model appears to be sufficient to provide an estimate of heating rate and corresponding pressure rise rate for use in defining the test parameters for the ‘real world’ test conditions.

2.1.2 Fired Heating of Propane Tanks

Numerous journal papers were found that considered the response of various sizes of propane tanks to different types of fire conditions. These articles presented experimental results, theoretical models, or combinations of the two.

According to the literature, when tanks of various sizes are exposed to fire conditions, the heat flux applied to the exterior of the tank is hundreds of W/m^2 [2]. This is at least 10 times the heat flux estimated by ambient conditions. The heat flux can vary significantly as it is dependent upon the fuel type, wind direction and speed, the overall size of the fire, and the location of the fire relative to the tank. The higher heat flux from a fire causes the uniform saturated liquid/vapor propane mixture at a single temperature assumption to no longer be a valid approach to modeling. The heat from a fire is conducted much more effectively to the liquid propane than the vaporized propane. As the heat enters the liquid propane, it begins to vaporize the liquid propane in close proximity to the tank walls. Thermal stratification and gradients result with the effect being that the bulk liquid temperature of propane may not change significantly even though the vapor pressure has increased dramatically. [2]

A summary of the literature for fired heating of propane tanks is in presented in Table 1. As can be seen from Table 1, the rate of pressure change in a fire scenario is closer to the values used in the original test program (0.5 psi/s). These values are 10 to 100 times greater than the predicted rate of pressure change under ambient and solar heating discussed in section 2.1.1. Therefore, the data presented in the literature on tank pressure rise rates in a fire are not representative of normal field conditions.

Table 1 - Summary of Fire Test Results

Reference	Overview	Fill	Content Source	Pressure Ramp Rate (psi/s)
3	500 gallon tank subjected to a 25% engulfing flame from side	Not specified	Experimental & Numerical	0.33 (1st test) 0.57 (2nd test) 0.57 (numerical)
4	Anecdotal report of pressure ramp rate	NA	Anecdotal	1.0-2.0
5	750 gallon tank subjected to a diesel pool fire	80% 50%	Experimental	0.04 (80% fill) 0.035 (50% fill)
6	1000 gallon tank subjected to structure fire from side and one end	80% (est.)	Numerical and Anecdotal	0.38
8	500 gallon tank subjected to a simulated 100% engulfing fire with propane burners	80%	Experimental	0.02

2.2 Elastomeric PRV Component Performance Considering Temperature

Another question arose during the development of the additional tasks regarding how the elastomeric sealing materials used in PRVs perform under elevated temperature conditions. To help answer this question, the online seal design guide available from Apple Rubber Products Inc. (http://www.applerubber.com/[2]) was reviewed to identify elastomeric materials suitable for

[2] http://www.applerubber.com/sdg/guide2/material_guide/src/compat.pdf
http://www.applerubber.com/sdg/guide2/material_guide/src/genprop.pdf

propane use and the recommended temperature limits of those materials. This information is summarized in Table 2.

The lowest maximum temperature rating for the elastomeric materials is 225°F (polysulfide) which is much higher than the temperature the PRV would reach when subjected to normal ambient heating. Therefore, there is minimal concern about the gasket being compromised due to normal heating in ambient conditions and should perform appropriately for their intended application. However, temperatures from a fire can far exceed the maximum temperature ratings for elastomeric materials and therefore it is not expected that these materials would withstand fire conditions.

Table 2 - Thermal Limits of Elastomeric Seal Materials for Propane Applications

Material	Exposure Rating Grade[3]	Low Temp Limit (F)	High Temp Limit (F)
Buna-N	Good	-85	275
Chemraz®	Good	-35	600
Epichlorohydrin	Good	-40	275
Fluorocarbon	Good	-40	400
Kalrez®	Good	-35	600
Nitrile, Hydrogentated	Good	-40	350
Polysulfide	Good	-50	225
Teflon®, Virgin	Good	-300	450
Vamac®	Good	-40	300
Fluorosilicone	Fair (Usually OK for static seal)	-85	400
Neoprene®	Questionable (Sometimes OK for static seal)	-45	250

2.3 Thermal Modeling of a Propane Tank

2.3.1 Thermal Model Overview

A simple thermal model for the ambient heating of a 500 gallon or 1,000 gallon propane tank was constructed using the same basis as de Nevers [1] to provide an estimation of the pressure rise in a propane tank due to daily weather fluctuations. Several iterations were performed to investigate the effect of different tank fill levels on the pressure rise rate during an average daytime/nighttime summer temperature in Arizona. Ultimately, the data derived from the thermal model is used as input to the 'real world' test conditions.

The model is a simple lumped parameter model for a cylindrical tank subjected to ambient weather heating and solar radiation. Specific assumptions include:

- Propane
    - Propane exists in the tank as a well mixed saturated liquid at the tank temperature.

[3] This refers to the suitability of the material for use in propane service.

        - For higher heating rates, it is well known that thermal stratification is an important effect and that the vapor pressure can be much higher than the saturation pressure of the bulk liquid temperature.
    - The working fluid is 100% pure propane
        - Impurities and additives will have a slight effect upon the propane thermodynamic properties used in the model (specific heat, saturation pressure).
    - The propane initial temperature and tank initial temperature are the same as the average ambient temperature over a 24 hour period.
- Tank
    - Tank has spherical end caps.
    - 500 gallon tank is 120 inches long, 37 inches in diameter, and weighs 950 lbs.
    - 1,000 gallon tank is 190 inches long, 41 inches in diameter, and weighs 1750 lbs.
    - The tank is approximated as a long cylinder to model the free thermal convection from the tank.
    - Tank liquid fill levels of 80%, 60%, 30%, and 10% are considered. The fill level is determined by the volume of liquid propane relative to the total volume of the tank.
    - Tank is made of plain carbon steel.
- Ambient Weather
    - The ambient temperature is approximated by a sine wave with a period of 24 hours.
    - The average daily temperature is 92.5°F. The maximum temperature is 114.8°F and the minimum temperature is 70.2°F.
        - These temperatures correspond to average conditions for Phoenix in July.
    - Ambient wind speed is 3 mph.
        - A higher ambient wind speed will increase heat gain to the tank from the ambient temperature while a lower wind speed will decrease heat gain to the tank.
- Solar Radiation
    - The solar flux is 365 W/m^2.
        - The literature review identified 200 W/m^2 to 485 W/m^2 as acceptable values for approximating the solar radiation from a clear sky in the western U.S.
    - The surface emissivity of the tank is 0.5.
        - The literature review found sources using values as low as 0.2 (reflective paint coating) to 0.9 (typical fire model).
    - 1/3 of the tank surface "views" and absorbs radiation from the sky.
    - Radiant heating is constant for a 12 hour period.
        - Although this is not the case, this assumption was required to make the model simple and solvable. Previous studies [1] have found this an acceptable assumption.

2.3.2 Modeling Results & Discussion

The pressure/temperature curves for the four propane fill levels in a 500 gallon tank over a 12 hour period are shown in Figure 1. The same curves are shown for a 1,000 gallon tank in Figure 2. The thermal responses of the 500 gallon tank and 1,000 gallon tank are fairly similar and therefore this discussion focuses on the general trends observed for both tanks.

The rate of pressure rise is highest for tanks with the lowest fill level. This is because the solar heat inputs and convective heat inputs are constant regardless of tank geometry and the propane is assumed to have uniform temperature inside the tank. A lower fill level corresponds to a lower thermal mass in the tank and therefore the faster response for a fixed input. In reality, the heat transfer through the portions of the tank wetted with liquid propane is higher than that through the portions of the tank exposed to vaporized propane.

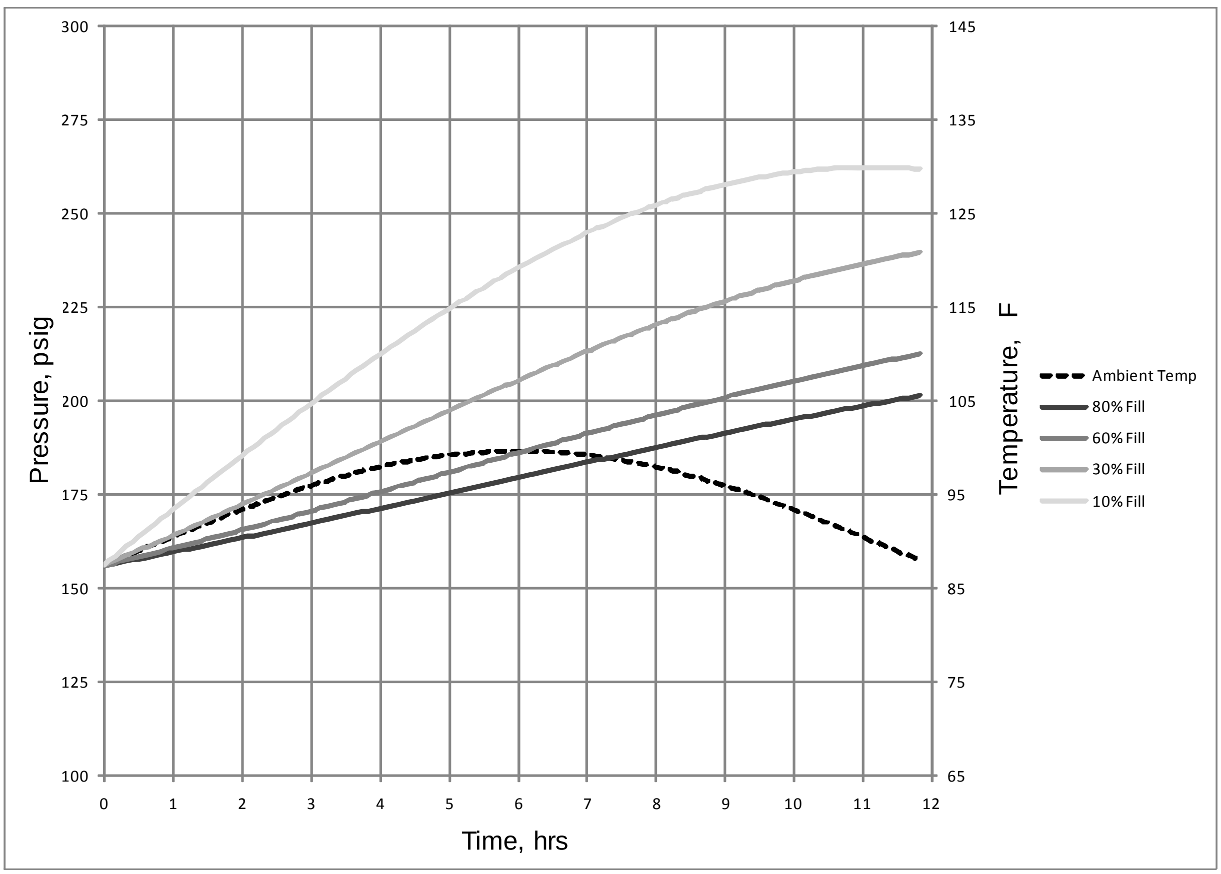

Figure 1 - Thermal Response of 500 Gallon Propane Tank

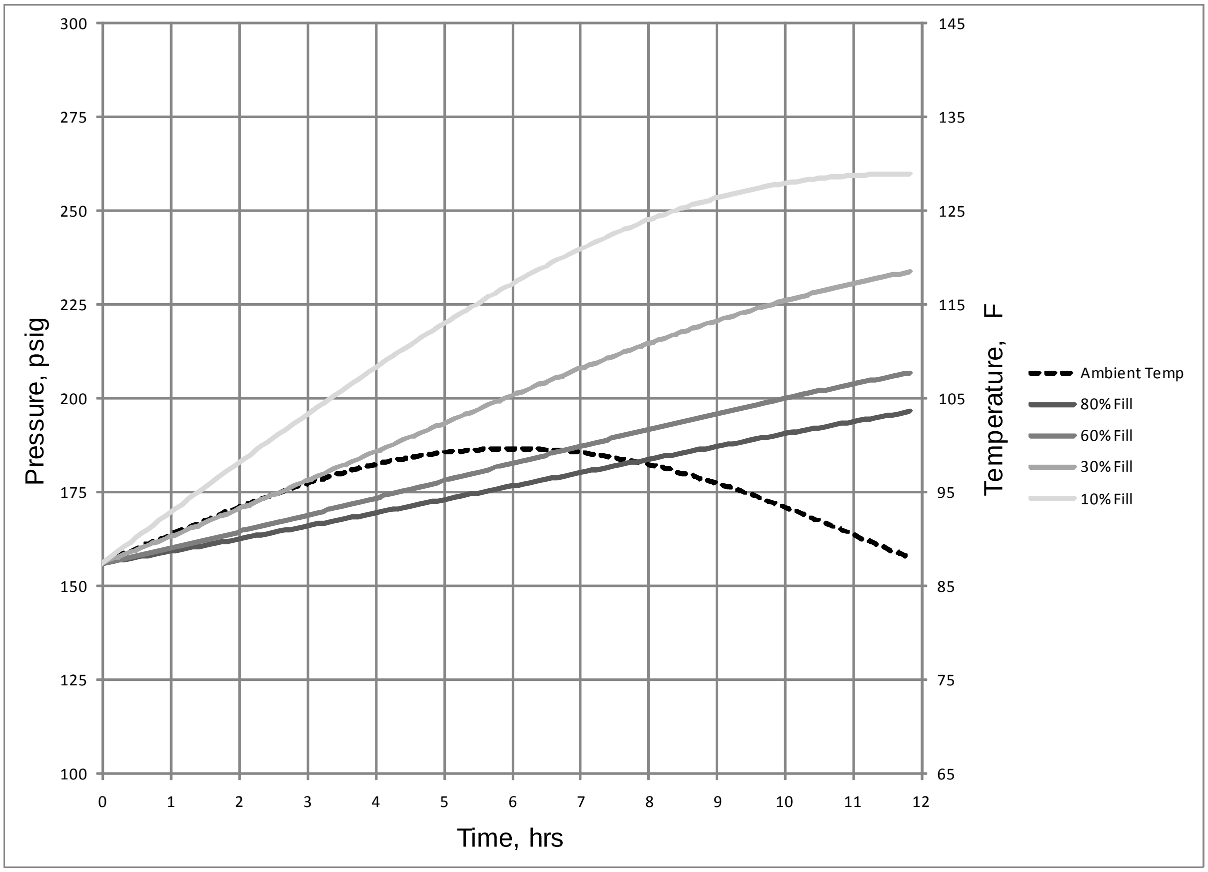

Figure 2 - Thermal Response of 1,000 Gallon Propane Tank

A summary of the modeled pressure rise rates is presented in Table 3. The pressure rise rate ranges from 0.0015 to 0.0032 psi/s depending on the fill level. These calculated rates are less than to those reported by de Nevers [1] for the smaller DOT containers exposed to ambient and solar heating, which is expected since our model is based on 500 and 1,000 gallon tanks.

Table 3 - Summary of Modeled Pressure Rise Rates

Tank Size (gal)	Fill (%)	Pressure rise (psi)	Rise Time (hrs)	Pressure Rise Rate (psi/sec)
500	80	70	12	0.0016
500	60	82	12	0.0019
500	30	106	12	0.0025
500	10	115	10	0.0032
1,000	80	64	12	0.0015
1,000	60	76	12	0.0018
1,000	30	102	12	0.0024
1,000	10	113	10	0.0031

A second noticeable observation is that the tank pressure continues to increase for some time after the ambient temperature has peaked. The tank pressure is driven by both convective heat transfer and solar radiation. As such, the thermal mass of the tank and the constant radiant heat input will result in the peak temperature being realized some time after the ambient temperature has peaked. For the 30%, 60%, and 80% fill levels in both Figure 1 and Figure 2, it would appear the pressure is still increasing at the end of the 12 hour period. However, this is an artifact of the model assumptions and not expected in actual operating conditions. At the end of 12 hours, the radiant heating is assumed to go to zero and the ambient temperature is still decreasing and therefore the temperature of the tank will not increase any further than what is indicated in the figures. If the model time period was extended to reflect the change in thermal inputs, a sharp bend would appear on the plots at 12 hours and the tank pressure would trend downward. As described in the model assumptions, typical radiant heating would not be constant over the 12 hour period as was assumed here to simplify the model. Instead, it would increase at the beginning of the 12 hour period and decrease towards the end, eliminating the sharp transition.

The idealized assumptions required to create a simple and solvable model are not realized in the field. For example, the natural and constant variation in wind speed and solar radiation parameters will affect the heating rate and corresponding rate of pressure rise.   Therefore the thermal model results should be used to understand the approximate magnitude of pressure rise rates in a tank subjected to ambient and solar heating conditions. Care should be taken in extracting these and other conclusions from the data.

2.4 Testing of Additional PRVs Simulating Real World Conditions

2.4.1 Overview and Setup

Based on the results of the literature review and thermal modeling, two experimental test procedures were created with the intent of simulating external conditions more representative of actual field conditions. A limited number of tests were run on 250-psig set point PRVs under each procedure to see if there was any indication that PRV performance varied based on the modified test procedure.

The first test procedure was designed to simulate the conditions under which a PRV must open to relieve pressure in an over-filled tank subjected to ambient heating. The two variables chosen for control were the rate of pressure rise and the temperature of the PRV. A pressure rise rate of 0.004 psi/sec (0.24 psi/min) was selected based on the literature review and thermal modeling to simulate about eight hours of constant pressure rise during ambient heating to reach the PRV set pressure. For comparison, the pressure rise rate used in the original test program was 0.5 psi/sec (30 psi/min). The temperature of the PRV was controlled to approximately 130°F to approximate the temperature of the PRV when subjected to solar radiation in a hot ambient environment. The temperature was selected to duplicate what the PRV might experience on one of the hottest days in summer in the southwest US. This was considered to be a fairly extreme condition that is regularly realized in the field.

The PRV was heated using a resistance heater clamped to the end of the PRV. Two thermocouples were applied to the exterior body surface of the PRV on the hex. One thermocouple was used for control of the heater and the other was used to record temperature. A relay controller in deadband control mode was used to maintain the PRV near the desired set temperature. A picture of the test setup is shown in Figure 3.

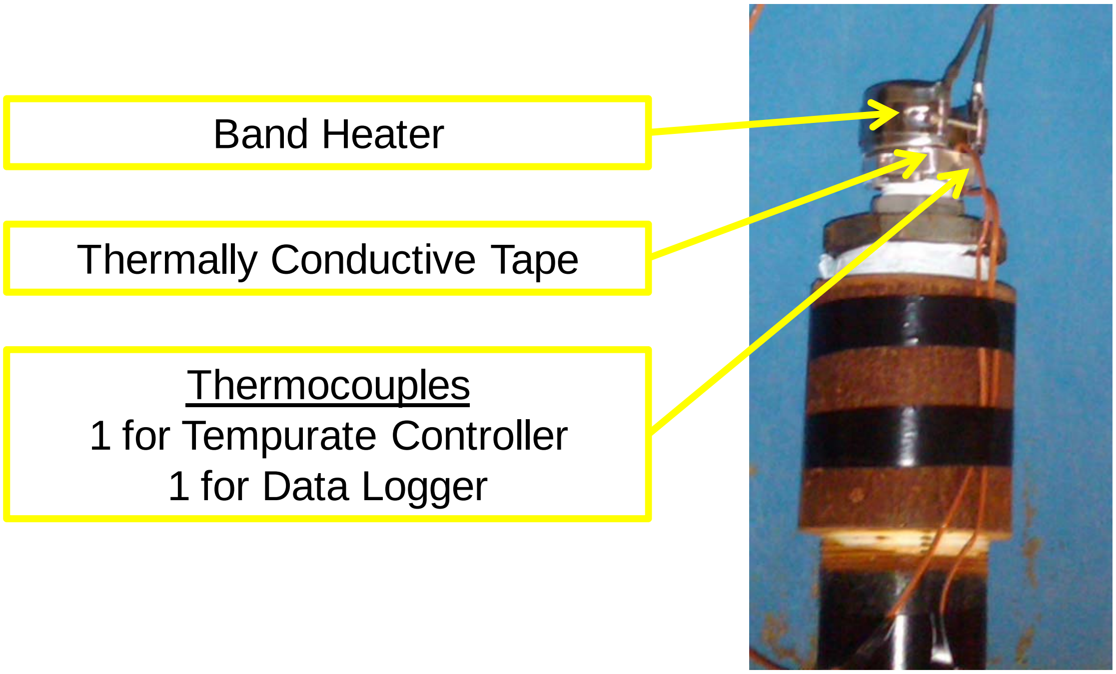

Figure 3 - Test Setup for Ambient Heating with Overfill Test

The second test procedure was designed to determine if conditioning the PRVs in a propane environment had any effect on the PRV performance. There was some concern in the original test program that the PRV start-to-discharge pressure may have been influenced by the lack of internal pressure to the PRV prior to testing. PRVs in the field have a constant pressure applied from the propane vapor pressure that acts to oppose the 250 psig spring force keeping the PRV in the closed position. The PRVs initially tested by Battelle had no applied pressure for several months (in the original test program) and over a year (in this additional work). Additionally, there was some speculation that propane conditioning may have some effect on the elastomeric seat disk material that enables better performance. Therefore tests were conducted as part of this task to determine if propane conditioning had an effect on PRV performance by testing a sample of PRVs using the original test protocol (a pressure rise rate of 0.5 psi/sec; no ambient heating) but conditioning the valves in propane for several weeks prior to testing.

The apparatus used to condition the PRVs in propane consisted of a small length of pipe from which the air was removed before filling with propane. Since there was not a large amount of liquid propane in the fill, the pressure inside the conditioning vessel varied with external temperature from about 90 psig to 110 psig. It was intended that the PRVs be conditioned for a minimum of one week prior to testing; however, due to an equipment failure on the test rig, the PRVs were conditioned for over one month.

2.4.2 Test Results

The main performance issues that were evaluated in the original test program included:

- PRV did not relieve by 375 psi
- PRV start-to-discharge pressure below the set pressure
- PRV start-to-discharge pressure higher than 120 percent of the set pressure
- PRV resealing pressure lower than 90 percent of the set pressure

The maximum test pressure was limited to 375 psi primarily for safety reasons and it also represents the hydrotest pressure for ASME tanks with a working pressure of 250 psi. The criteria specifying a start-to-discharge pressure higher than 120 percent of the set pressure was selected as this represents the pressure at which a new PRV should be fully open according to UL 132. The two additional criteria (start-to-discharge lower than the set pressure and resealing pressure lower than 90 percent of the set pressure) were chosen since they represent potential chronic leak and safety issues for a PRV.

This new test program evaluated a narrow data set of 14 PRVs under various more 'real world' conditions, including elevated temperatures (130°F), slow pressure rise rate (0.004 psi/s), and/or propane conditioning prior to testing. Three sets of tests were conducted 1) a sample of four previously untested PRVs and two previously tested PRVs that were found to be 'stuck' shut at 0.004 psi/s and 130°F; 2) a sample of two previously untested PRVs and one previously tested PRV that was found to be 'stuck' shut with propane conditioning of the valves; 3) a sample of five previously tested PRVs that were found to be 'stuck' shut at 0.004 psi/s, 130°F, and propane conditioning.

<u>Test Set 1: Slow Pressure Rise and Applied Heat</u>: Six 250-psig set point PRVs were tested using a slow pressure rise rate and external heating. The test matrix was comprised of two newer untested PRVs (<20 yrs old), two older untested PRVs (>20 yrs old), and two previously tested PRVs that were found to be 'stuck' shut. The untested PRVs were included for comparison and verification of the proper test procedure. One of the stuck PRVs was unconditioned (PRV 326) and the other was conditioned in a propane environment for over one month (PRV 274).

The testing was started manually and ran unattended until completion since each test could take over 15 hours to complete due to the slow rate of pressure rise. Therefore the criteria for a PRV opening was not visual observation of bubbles emanating from the PRV as had been the case for the original project. Rather, a flow meter in line with the PRV was used to determine when the PRV opened. A bubbling air flow is below the measurement threshold for the flow meter so the reported opening pressures correspond to the PRV being opened more than just a small amount to produce bubbling. The difference in pressure between bubbling and higher flows is generally only a few psig as found out in the original test program [19]. The test data was analyzed to identify where there was a slow open versus a popping of the PRV. A slow open would have multiple flow readings within the measurement range of the flow meter and a relatively constant PRV inlet pressure. A PRV that popped open would have multiple flow readings at the maximum of the air flow meter and a substantial drop in PRV inlet pressure.

As shown in Table 4 all PRVs tested under these conditions opened, including those that were previously found to be 'stuck' shut. Three of the PRVs, all at least 30 years old, exhibited high start-to-discharge behavior with opening pressures higher than 275 psig (the UL 132 start-to-discharge criteria for new 250-psig set pressure PRVs).

Table 4 - Results of New Test Procedure (Slow Pressure Rise and Applied Heat)

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Opening Type
475	Internal	3/4"	9	No	246	Slow open
49	Internal	3/4"	17	No	252	Slow open
208	Internal	3/4"	28	No	271	Popped
394	Internal	3/4"	30	No	327	Popped
326	Internal	3/4"	45	Yes, Stuck	355	Popped
274	Internal	3/4"	43	Yes, Stuck	328	Popped

Test Set 2: Propane Conditioning (original test protocol): Another three 250-psig set point PRVs were conditioned in a propane environment and tested using the original test procedure. The original procedure includes increasing pressure at 0.5 psi/s, no external heating of the PRV, and the visual observation of bubbling as indication that the PRV opened. Like the original test program, the test procedure was repeated three times in close succession for each PRV. The test results are summarized in Table 5. All three PRVs opened under this test procedure. Two of the PRVs still had high start-to-discharge pressures; both of which were greater than 20 years old (one was determined to be 'stuck' closed in the previous test program).

Table 5 - Results of Original Test Procedure with Propane Conditioning of PRVs

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Reseat Pressure (PSIG)
484	Internal	1"	10	No	264	264
					267	266
					268	267
407	Internal	1"	32	No	329 (Popped)	---
					287	260
					287	259
350	Internal	1"	22	Yes, Stuck	352	314
					327	311
					323	308

Test Set 3: Slow Pressure Rise, Applied Heat, and Propane Conditioning: To increase confidence in the test results, an additional five 250-psig set point PRVs were tested. All five of these PRVs had been tested in the original test program and found to be stuck shut. The five PRVs were conditioned in propane for at least four days prior to testing and then subjected to the test procedure with a slow pressure rise and external heating. The intent of the additional testing was to increase confidence that the new more 'real world' test conditions consistently resulted in improved PRV performance.

The test results are summarized in Table 6. Four of the five previously tested and 'stuck' shut PRVs opened under the new test conditions and all four exhibited high start-to-discharge pressures (> 275 psig). One PRV remained stuck after reaching the test limit of 375 psig. This valve was further pressurized to 500 psig without opening (at this pressure the test was terminated for safety concerns). All PRVs tested in this group were greater than 40 years of age.

PRV 62, which did not open under the new test conditions, was subsequently examined in the failure analysis task (Task A3). During that examination, severe corrosion was found such that the spring was chemically bonded to the valve body and a load of 832 pounds was required to free the spring and sleeve from the valve body. It should be noted that PRV 62 is an external type valve which are no longer installed on new tanks.

Table 6 - Results of New Test Procedure (Slow Pressure Rise and Applied Heat) on Additional Stuck Valves with Propane Conditioning

PRV	Internal/ External	Size	Age (Years)	Previously Tested	Opening Pressure (PSIG)	Opening Type
175	External	3/4"	40	Yes, Stuck	345	Popped
173	Internal	3/4"	44	Yes, Stuck	347	Slow open
102	Internal	1”	52	Yes, Stuck	308	Slow open
62	External	3/4"	57	Yes, Stuck	Did not open	
10	Internal	1”	58	Yes, Stuck	285	Slow open

2.4.3 Results Discussion

Figure 4 compares the initial start-to-discharge pressure to the performance criteria and age for the 250-psi set point PRVs tested in this program. The vertical axis is the parameter tested (pressure) while the horizontal axis is an indication of the age of the PRV tested. The colored horizontal lines represent the start-to-discharge, full open, resealing, and blow-down pressure limits as specified in UL 132. The different data symbols represent the test variables used for that particular valve (O = conditioned, 0.5 psi/s, not previously tested; Δ = not conditioned, 0.004 psi/s, stuck PRV; X = not conditioned, 0.004 psi/s, not previously tested; □ = conditioned, 0.004 psi/s, stuck PRV; + = conditioned, 0.5 psi/s, stuck PRV). The darker gray band represents the range of acceptable PRV performance per UL 132. Data points that are circled with the label ‘DNO’ signify PRVs that did not open by 375 psi. Significant differences between ages are evident by the variation in the vertical spread of the data points.

The results for the new test conditions show that PRVs less than 20 years old generally performed within the UL 132 criteria for new valves (with one opening 2 psi lower than its set pressure). One 22 year old PRV had high start-to-discharge and resealing pressures. When this valve was examined, it was found to have the highest spring load and load-displacement value of all PRVs with comparably sized springs (see Section 4.1). The high spring load caused by a higher load-displacement value and a greater installed displacement may indicate that the PRV factory set pressure was set high. All PRVs 30 years old and greater opened at high start-to-discharge pressures (>275 psig).

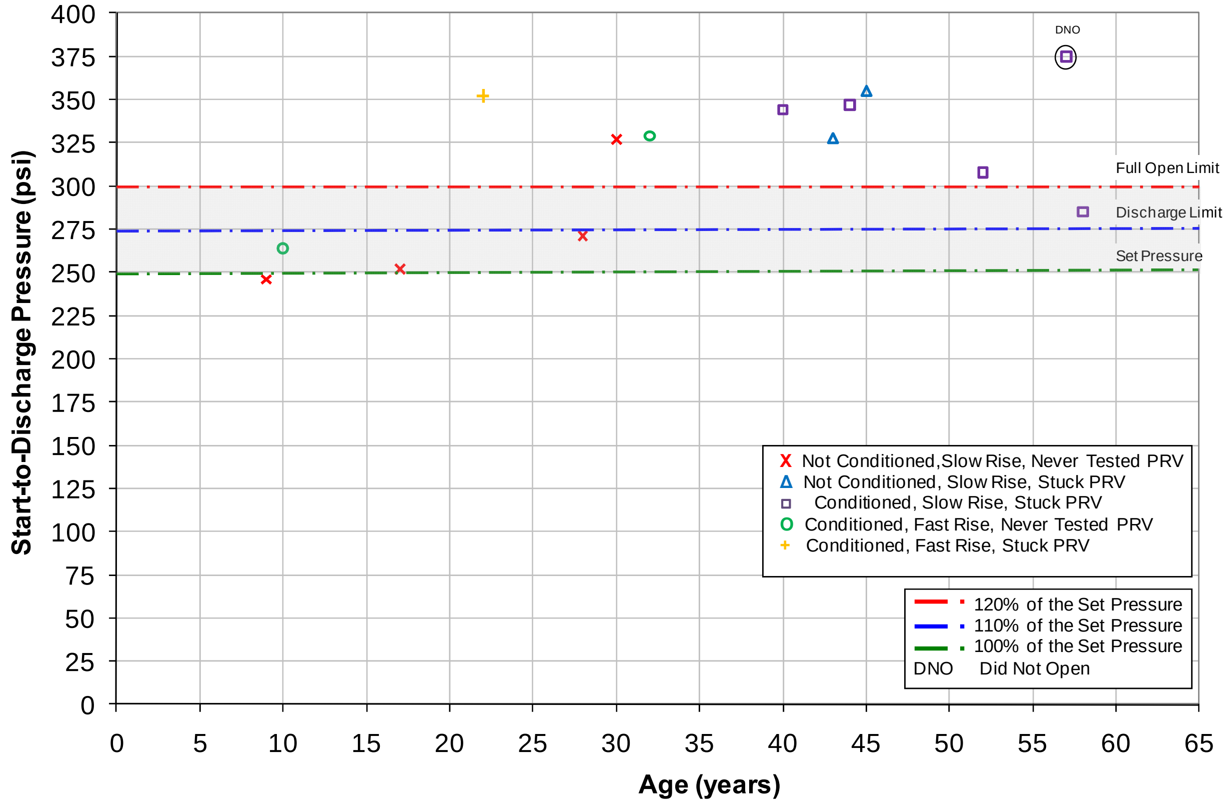

Figure 4 - Results of All Additional Testing for 250-psig Set Point PRVs

Of the eight previously stuck PRVs tested, seven opened under the new test conditions indicating that propane conditioning, heating, and/or low pressure rise rates have an influence on the performance of PRVs removed from the field. All seven of the previously 'stuck' closed PRVs that opened under the new test conditions still exhibited high start-to-discharge pressures (in excess of 110 percent of the set pressure) but opened within 1.5 times the set pressure (hydrotest pressure for ASME tanks with a working pressure of 250 psi). Additional analyses of PRV 62 (external type valve no longer installed on new tanks) indicated severe corrosion caused it to remain stuck under the new test conditions.

The new experimental test results indicate that 'real world' conditions make a difference in how the PRVs perform for this limited data set and they still show a deterioration in performance based on the age of the PRV which increases for PRVs 30 years old and older.

2.5 Review of Propane Tank Codes and Other Pressure Vessel Design Margins

The objective of this task is to review the design factors for propane tanks and other comparable pressure vessels to identify if there are differences in the design margins and if so, why and what is the significance.

The ASME Boiler and Pressure Vessel Code (BPVC) sets the rules for design, fabrication, and inspection of pressure vessels. Section VIII, Division 1sets forth the design rules for pressure vessels (both fired and unfired) operating at internal or external pressures in excess of 15 psig. Residential propane tanks are designed in accordance with Section VIII, Division 1 rules which do not differentiate design margin based on service conditions, working fluid, or materials (i.e. a propane tank is designed to the same rules as other pressure vessels including air tanks and boilers).

The basic approach of the BPVC Section VIII, Division 1 is to give simple equations and rules for the design and testing of pressure vessels without detailed consideration of the nuances of the design. For example, a propane tank is considered to be a simply supported cylindrical vessel with semispherical or ellipsoidal end caps; localized stresses due to details of the supports, ports, or other tank features are neglected. This approach is facilitated by the use of a material Design Factor. The raw material Ultimate Tensile Strength is divided by the Design Factor to determine the maximum allowable material stress. The maximum allowable material stress is used in conjunction with basic loadings, the vessel geometry, and the design pressure to determine the Maximum Allowable Working Pressure (MAWP) of the vessel, which for ASME propane tanks is 250 psig. The MAWP in turn determines the hydrostatic test pressure and the pressure relief requirements for the vessel. The start-to-discharge pressure setting for PRVs is to be 100 percent of the container MAWP [20], which is equivalent to 250 psig[4]. This process is depicted in Figure 5.

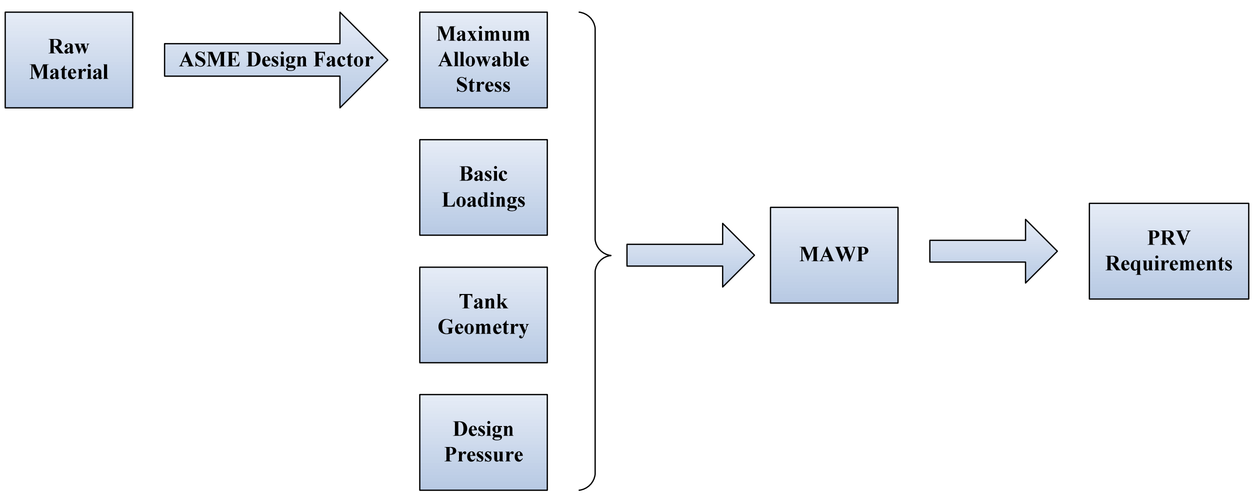

Figure 5 - ASME BPVC Section VIII, Division 1 Design Flowchart

For example, consider a propane tank made from ASME SA-455 carbon steel plate with a design pressure of 250 psig and a design temperature is 70°F. ASME BPVC Section II (Materials) Table U specifies an Ultimate Tensile Strength of 75,000 PSI. Table 1A specifies a Maximum Allowable Stress of 21,400 PSI. The Maximum Allowable Stress is equivalently determined by dividing the Ultimate Tensile Strength (75,000 PSI) by the Design Factor (3.5). Formulas specified by the ASME BPVC use the specified design pressure of 250 psig, the Maximum

[4] Manufacturers of PRVs are allowed a plus tolerance not exceeding 10-percent of the set pressure marked on the valve.

Allowable Working Stress of 21,400 PSI, and the radius of the tank to determine the required material thickness for the tank. The MAWP is taken to be the design pressure of the tank.

For a hypothetical cylindrical vessel with spherical end caps subjected only to internal pressure, the maximum stress realized in the vessel wall would be the same as the Maximum Allowable Stress and this would be well below the Ultimate Tensile Strength of the vessel material. One could then infer that the vessel is overdesigned (by the design factor of 3.5 if no factor of safety is utilized). For a real propane tank, additional loads (wind, bending, etc.) and stress concentrators (supports, ports, etc.) will increase the maximum stress realized in the vessel wall above the Maximum Allowable Stress. This is quite acceptable since the design factor is chosen such that these unknown factors keep the maximum actual stress below the Ultimate Tensile Strength including some factor of safety.

2.5.1 Historical Perspective on BPVC, Section VIII, Division 1

A design factor of 5 was used in the first publication of Section VIII of the ASME BPVC in 1925. The design factor was reduced to 4 in 1945 due to the availability of better materials, more restrictions on fabrication, better fabrication methods[5], and improved nondestructive examinations. From 1955 through 1968 Section VIII, Division 2 rules were written to support equipment and processes in the petrochemical industry. Section VIII, Division 2 uses a design factor of 3. This is facilitated by more restrictive rules, more detailed design, and more nondestructive testing relative to Section VIII, Division 1. In 1999, the design factor for Section VIII, Division 1was reduced to 3.5. This was driven by the desire to reduce the cost of construction, be more consistent with European designs with a good safety record, and take advantage of various code improvements[6] since the sixties [9].

The design factor is not equivalent to a factor of safety. The design factor is used to allow for simple design calculations that consider the general loading on the tank without consideration of specific geometrical details, localized stresses, or stress concentrating features. A factor of safety is the ratio of the known maximum stress to the appropriate material limit. Over the years, the design factor has been reduced with each reduction justified by technological improvements. The tradeoff has been such that the safety factor on the tank has been perceived to remain relatively unchanged over the years [10].

2.5.2 NFPA 58 Recommendations for Testing Relief Valves

Appendix E of NFPA 58, Liquefied Petroleum Gas Code, provides guidance on testing PRVs for ASME containers. Section E.2.3 specifies that frequent testing of pressure relief valves on LP-Gas containers is not considered necessary for several reasons: 1) LP-Gases are ‘sweet gases’ having no corrosive or other deleterious effect on the metal of the containers or relief valves; 2) the relief valves are constructed of corrosion-resistant materials and are installed so as to be protected against the weather. The variations of temperature and pressure due to atmospheric conditions are not sufficient to cause any permanent set in the valve springs; 3) the required

[5] According to NFPA 58, Appendix D, fabrication changed from the riveting widely used when the code was first written to fusion welding. This latter method was incorporated into the code as welding techniques were perfected and now predominates.

[6] According to NFPA 58, Appendix D, these include improvements in metal manufacturing, welding techniques, X-ray quality, and pressure vessel manufacturer’s quality systems.

odorization for the LP-Gas makes escape almost instantly evident; and 4) experience over the years with the storage of LP-Gases has shown a good safety record on the functioning of pressure relief valves [20].

Appendix E of NFPA 58 further states that because no mechanical device can be expected to remain in operative condition indefinitely, it suggests that the pressure relief valves on containers greater than 2,000 gallons water capacity be tested at approximately 10-year intervals [20].

3.0 PROPANE INDUSTRY SURVEY TO DOCUMENT PRV INCIDENTS IN THE FIELD (TASK A2)

Although the results from the original test program showed inconsistent PRV performance against the UL 132 criteria for new valves, anecdotally PRVs have a good safety record in the field and there is little information or reports of problems to be found in the literature. The intent behind Task A2 was to survey propane industry experts, review literature, and conduct web searches to see what information on PRV incidents was available.

Fifteen members of the propane industry representing a cross section of PRV manufacturers, tank manufacturers, researchers, and those involved with propane industry programs (e.g. PERC Safety & Training) were contacted by Battelle. The type of data requested from these sources included ASME tank failures, especially if there was documentation that the PRV was noted to be (or not to be) functioning, and other documented PRV incidents for various sizes of valves (i.e. ASME tanks, cylinders, transports). This information was supplemented with limited web searches and literature for the same type of data. The persons contacted are listed in Table 7 which includes their response, if provided.

Table 7 - Contacts to Quantify PRV Field Failure Data

Affiliation	Response
General Industry Contacts	
PERC Safety & Training	Although PERC maintains a database of propane incidents, there is not sufficient granularity in the information to identify specific failures related to PRVs.
Consulting Solutions, LLC	Recounted two incidents (1) fork lift cylinder on which the PRV had been filled with cement dust and therefore was unable to open (2) failure of a transport truck tank on which the PRV was packed with debris. Also stated that he is aware of more than a hundred situations where for a variety of reasons, including overfilling or overheating, that relief valves have opened. In his 33 years of dealing with millions of propane storage tanks, he is not aware of a single incident of a static tank failure or any failure related to a PRV not opening.
Propane Gas Defense Association	No responses received from e-mail request sent to the PGDA membership. The president and long-time member of the PGDA did report to Consulting Solutions, LLC that he was not aware of any PRV failures.
Propane Industry Incident Investigator	Recounted three incidents relevant to this study including (1) sulfide stress cracking of PRV spring due to off-specification product led to its failure in a 30,000 gallon bulk tank (2) failure of 15,000 gallon bulk tank in which it was suspected the PRV was plugged with ice (3) eye injury when a customer tried to close a PRV that had opened
Compressed Gas Association (CGA)	None

Affiliation	Response
PRV Manufacturers	
ECII/RegO	Unable to supply any information due to its confidentiality.
Sherwood	Did not have any data on PRV incidents available to provide to Battelle.
Fisher	Fisher has not manufactured domestic tank type relief valves for several years (probably since 1998) and no longer has any history of PRV returns. Only three incidents related to domestic tank valves for products built in 1972 and 1973 were found. Two of the three involved relief valve discharges while people were looking over the valve. On one of the tanks, the tank was overfilled and seeping at the time the person looked over the relief valve.
Tank Manufacturers	
Quality Steel	No records of any pressure relief valve failures and qualified that if it is happening it is outside of their five year warranty period and the dealer is taking care of the replacement without notifying them. He has heard of relief valves popping off and then reseating themselves but sporadically at best. He further qualified that this is usually caused by overfilling the tank or product quality issues.
Trinity Tanks	Recounted one incident from 2003 in which a pressure relief valve failed from exposure to H2S after a molecular sieve malfunctioned at a refinery causing the propane to be high in H2S.
Liberty Tanks	Does not keep this type of data and suggested contacting Worthington Cylinder Corporation.
Worthington Cylinder Corporation	CGA captured PRV's from forklift cylinders and tested them to the CGA test protocol (pressurization rate, first bubble and reseal) in the 80's. Depending on the size of the valve, CGA found vulcanization and tearing of the seals occurred. The outcome was the requirement for replacing PRVs that is in CGA S-1.1. This data is no longer available by CGA. Mentioned that very similar testing was conducted by the Ontario Research Institute and Transport Canada resulting in very similar results (reports could not be obtained for review).
Canadian Propane Industry Contacts	
Queen's University in Canada	Does not have data related to field failures of PRVs and he made no indication whether or not he was aware of any field failures.
Transport Canada	No response.
Superior Propane	They have addressed the issue of historical catastrophic PRV failures with a regulator in Canada and felt that he should be able to provide us with the information to the regulator. Never received additional information.

Dr. Mike Birk of Queen's University in Canada has conducted several test programs for Transport Canada evaluating the performance of transport vessel PRVs under ambient conditions and simulated fire impingement conditions. Although Dr. Birk indicated through correspondence that he does not have data related to field failures of PRVs, his papers do discuss some issues related to PRV performance during fire testing. In particular, Petherick and Birk

[11] conducted a literature search to find the state-of-the-art for PRV design, testing, and modeling. The authors discuss several papers related to experimental studies, modeling studies, maintenance programs and tank fire engulfment tests.

Petherick and Birk [11] discussed that there is very little information regarding PRV performance during emergency releases and the information that is available has been obtained during controlled fire tests of pressure vessels in which the transient pressures within the vessels are monitored and recorded. The authors discuss that by analyzing this data, PRV performance can be determined. In several cases during these fire tests they found that “the PRVs have performed poorly” [11]. The authors cited a paper by Appleyard that measured the pressure-time history when LPG containers were exposed to fire. They reported that “during two of the tests, the PRV failed in the open position, causing all the vessel-contents to be released to the environment. During one of the other tests, the PRV cracked open for some unexplained reason. It remained in this cracked open position until the set pressure was attained, at which time it began to cycle in the expected fashion” [11]. In the cases cited, the effects of the fire likely caused the variable PRV performance.

The authors also cited fire tests conducted by Moodie et. al., in which “it was observed that in one of the five tests, the relief valve cycled once before failing in the closed position. The failure allowed the internal pressure and the vapor space wall temperature to rise uncontrollably. When the vessel finally ruptured, the internal pressure had reached 35 bar (508 psi) and the maximum wall temperature was approximately 600°C. Moodie et. al. (1985) was unable to establish the cause of the relief valve failure. During the other four tests the relief valves remained in the open position until the internal pressure was eventually down to atmospheric or thereabouts. This fail safe behavior was, upon subsequent examination of the valves, attributed to fire damage to the valve seats and to a weakening of the valve springs.”[7]

Details of specific PRV and/or propane container incidents found during this review are provided in Table 8. If the incident involved issues related to the PRV it is noted in the last column of the table. These incidents represent what was provided by the industry contacts listed above and from web searches and literature reviews for similar information. Because specifics are unknown for several of the incidents it is difficult to discern if some of the reported failures are actually the same event (e.g. the catastrophic PRV failures due to exposure to high H2S concentrations).

[7] The papers by Appleyard and Moodie cited by Petherick and Birk [11] were not reviewed separately so the details of the reported PRV failures could not be confirmed.

Table 8 - Propane Tank or PRV Incidents

Incident	Date	Location	Description	PRV Related?
PRV failure in 30,000 gallon bulk tank emptying tank contents	Unk	Hot Springs, SD	Catastrophic failure of PRV released contents of a 30,000 gallon bulk tank; did not result in a fire. The cause of the PRV failure was attributed to sulfide stress cracking of the spring. Contributing causes were attributed to the purchase of off-spec, 'over-odorized' propane which contained high amounts of H_2S. A total of four tanks were filled with the off-spec product. All except one PRV in these tanks showed signs of cracking. The one PRV that did not crack had a protective coating on the spring (phone conversation with propane industry incident investigator).	Yes
Eye injury when customer attempted to close open PRV	Unk	CA	Injury incident in which a propane customer found the PRV on his propane tank leaking. The customer attempted to stop the leak by inserting a screw driver into the PRV. The PRV discharged causing an eye injury. Initial investigation determined that the tank had been filled the same day and was located in a hot, desert-like environment. From all indications, the PRV was properly functioning; however it could not be determined if the tank had been overfilled (phone conversation with propane industry incident investigator).	Unk
Injuries when people were looking over PRVs as they discharged	1972-1973	Unk	Two incidents involving relief valve discharges while people were looking over the valve (email from Fisher contact).	Unk
Catastrophic failure of 15,000 gallon bulk tank	1/31/1993	Gwinner, SD	Catastrophic failure of 15,000 gallon propane tank in an overfill situation at the Melroe Company Manufacturing Plant. The propane system consisted of five large tanks--four with 30,000 gallon capacities each, and one with a 15,000 gallon capacity. These five containers were manifold together which enabled them to operate as one storage system. Each tank had its own shut-off valve so that any one tank could be shut off or isolated from the rest of the system. A fuel delivery of nearly 9,000 gallons was made on January 25, 1993. Before pumping the propane into the manifold, the operator noticed the 15,000 gallon tank was registering 97% full and was instructed to close the shut-off valves to the tank, deliver the fuel to the system and reopen the valves. This same procedure was followed during deliveries on January 27 and January 29 even though the 15,000 gallon tank was still registering 97% full. As of the January 29 delivery, no one had taken measures to correct the problem. By January 31, the outside temperatures had warmed from below zero to above freezing. At about 6 a.m.	Yes

Incident	Date	Location	Description	PRV Related?
			on the morning of January 31, the 15,000 gallon tank ruptured and began releasing its contents. The ensuing explosion and fire caused nearly $2 million in damage to the Melroe plant and surrounding neighborhood. At trial, the plaintiffs' theory (Melroe) was that the tank was overfilled then isolated from the rest of the system. Moreover, because the rain caps were missing from the pressure relief vents, they became blocked with snow and ice preventing them from releasing excess pressure. The overfilled isolated tank, they argued, combined with a dramatic rise in temperatures, created hydrostatic pressure inside the tank which ultimately caused the tank to fail at pressure levels much higher than it was designed to withstand. The defendants' theory (Gwinner Oil) was that the tank failed as a result of a defective weld which, over time, weakened and burst at pressures much lower than 250 psi--the pressure at which the relief valves were calibrated to activate (http://openjurist.org/125/f3d/1176) [13].	
BLEVE of a 1,000 gallon propane tank	10/2/1997	Carthage, IL	The U.S. Fire Administration investigated a propane tank explosion that killed 2 volunteer fire fighters on October 2, 1997 (USFA-TR-120). A release and ignition of propane occurred either from the failure of a corn dryer or failure of a flexible propane hose and exposed two 1,000 gallon tanks to excessive heat from the flames. One witness indicated that a pressure relief valve began to operate intermittently producing a loud noise and flames 40 to 50 feet high (expected PRV behavior in a fire). After some time the east tank BLEVE'd killing the two fire fighters and causing significant damage to surrounding buildings [16]. http://www.usfa.dhs.gov/downloads/pdf/publications/tr-120.pdf	No
BLEVE of an 18,000 gallon propane tank	4/9/1998	Albert City, IA	Herrig Brothers Feather Creek Farm – U. S. Chemical Safety and Hazard Investigation Board investigated the explosion/BLEVE of an 18,000 gallon propane tank that took place on April 9, 1998 and resulted in the death of 2 volunteer fire fighters and injuries to 7 emergency responders. The incident was initiated when two teenagers, riding an ATV, struck two aboveground propane pipes (liquid and vapor lines) that ran parallel to one another from the propane tank to direct-fired vaporizers used for heating turkey barns. The excess flow valve on the liquid line failed to function and the released propane eventually found an ignition source (likely the direct-fired vaporizers). A fire began to burn vigorously under the tank and continued until the tank ruptured (approximately 20-30 minutes later). During the fire, emergency responders noted that the noise from the pressure relief valves was "like standing next to a jet plane with its engines at full throttle" (expected PRV behavior in a fire) [18]. http://www.aristatek.com/Newsletter/JAN09/TechSpeak.pdf	No

Incident	Date	Location	Description	PRV Related?
BLEVE of 2,000 gallon propane tank		Truth or Consequences, NM	Cortez Gas Company – This incident (no causalities) involved a pickup truck that rolled into a propane storage yard and severed the plumbing system beneath an 18,000 gallon propane storage tank that was 85% full. The ensuing fire enveloped a nearby 2,000 gallon propane tank and two empty propane delivery trucks parked in the yard resulting in the BLEVE of the 2,000 gallon tank. Two PRVs (250 psi set pressure) were located on top of the tank and appeared to have functioned appropriately prior to the BLEVE [14]. http://www.springerlink.com/content/k544652621867q11/.	No
Failure of PRV on fork lift cylinder to open	Unk	Unk	Fork lift cylinder on which the PRV had been filled with cement dust and therefore was unable to open (Consulting Solutions, LLC).	Yes
Catastrophic failure of transport truck tank	Unk	Unk	Failure of a transport truck tank on which the PRV was packed with debris. When the PRV was tested it still did not open even after reaching 1200 psi. The tank was ~10 years old but had not been inspected at its regular 5 year interval (Consulting Solutions, LLC).	Yes
PRV failure emptying contents of tank	2003	Unk	A pressure relief valve failed from exposure to H_2S after a molecular sieve malfunctioned at a refinery causing the propane to be high in H_2S (Quality Steel).	Yes
BLEVE of propane tank during fire testing	Unk	Unk	Petherick and Birk [11] cited pressure vessel fire testing conducted by Moodie et. al. in which a PRV cycled once before failing in the closed position. The failure allowed the internal pressure and the vapor space wall temperature to rise uncontrollably. When the vessel finally ruptured, the internal pressure had reached 35 bar (508 psi) and the maximum wall temperature was approximately 600°C. Moodie et. al. (1985) was unable to establish the cause of the relief valve failure.	Yes

Based on the data in Table 8, Battelle was able to document six PRV related incidents. Three documented incidents were due to a PRV being stuck shut (blockages from ice or debris); two incidents were due to PRV exposure to off-specification product high in H_2S in which the valve spring cracked and failed; one incident was from an unknown cause in which the PRV on a propane vessel failed in the closed position during a fire test of the vessel. The root causes for five of the six incidents were attributed to external factors (off-specification product or valve blockages), not the manufacture or age-related deterioration of the PRV. The cause of the sixth incident was unknown and the report documenting this incident was unavailable for review.

Three incidents were reported in the literature in which storage tanks ranging in size from 1,000 gallons up to 18,000 gallons BLEVE'd in a fire. All three incidents reported that the PRVs had relieved per their intended design.

There were also three incidents reported where a PRV discharged while someone was looking over the PRV causing them injury. These last three incidents were not included as part of the PRV incident data as there was not enough information to discern if the tank was overfilled causing the PRV to relieve per its design or if there was another issue with the PRV.

To understand the PRV incident rate in the field, we also need to know the number of PRVs in service and their service life. Table 9 presents a rough estimation of the propane tank population (and therefore PRV population) based on the number of customers reported on the NPGA website and estimates of tanks per customer provided by Consulting Solutions, LLC. These estimates indicate there are over 12 million PRVs in service throughout the U.S.

Table 9 - Estimation of the Number of Propane Tanks in the U.S.

Customer Type	# of Customers[8]	Estimated # of Tanks per Customer	Total # of Tanks
Residential	9,720,000[9]	1	9,720,000
Commercial	1,040,000	1.1	1,144,000
Industrial	240,000	0.95	228,000
Fork-lift	456,000	Avg 3 units on site x 25% fill on site	38,000
Fleet Motor Fuel	81,000	Avg 8 units centrally fueled	10,125
Agricultural	660,000	1.4	924,000
Standby	110,000	0.95	104,500
Total			**12,168,625**

Considering there are over 12 million propane tanks currently in use and a maximum of six incidents that could be documented from this review (five of which were attributed to external factors), the known incident rate for PRVs in the field is low.

[8] Source: http://www.npga.org/i4a/pages/index.cfm?pageid=633
[9] The NPGA website lists this number as 14,300,000; however the PERC market metrics indicates this number is more around 9,720,000 http://www.propanecouncil.org/uploadedFiles/propanecouncil/PDFM/Propane%20Market%20Outlook%20_%20Full%20Report(1).pdf

4.0 PRV Design Review and Additional Failure Analyses (Task A3)

Battelle conducted a failure analysis of select PRV's that did not meet the performance requirements from the original test program to determine possible mechanisms and variables that may have contributed to the observed behavior. As stated previously, the performance requirements were based on UL 132, Section 11 which establishes operating parameters for newly-manufactured PRVs and a maximum test pressure of 375 psig which represents the tank hydrotest pressure (1.5 times the working pressure).

The valve selection process for failure analysis involved reviewing the PRV data generated during the 2009 study [19] to select a distribution of PRVs based upon their behavior during the performance testing; i.e., valves that did not open (DNO), valves that exhibited high start-to-discharge pressure (high s-t-d), valves that exhibited low start-to-discharge pressure (low s-t-d), and valves that opened within the set pressure tolerance range. In addition, the valves that exhibited abnormal behavior were classified by manufacturer, service environmental conditions, ages, and valve types (internal versus external) to select PRVs for failure analysis in proportion to those characteristics. For example, the review revealed that there were 25 valves that did dot open, 94 valves that exhibited high-start-to-discharge pressure, and 108 valves that exhibited low-start-to-discharge pressure. The remainder opened at pressures within the set point tolerances. It also revealed that about 50 percent of all of the PRVs tested were made by one manufacturer (Manufacturer A). Manufacturers B and C accounted for 15 and 21 percent of the PRVs tested in the original program. Focus of the failure analysis was placed on 250-psig set point, internal PRVs as these dominated the samples received for testing and are the predominant types of valves used for residential tank applications.

It was initially planned to conduct detailed examinations on all 25 of the valves that did not open during the initial test program. All of those valves were examined visually; however, it was mutually agreed between PERC representatives and Battelle to instead retest five additional 'stuck' closed valves from the initial study using the test protocols described in Section 2 of the present report. Consequently, not all of the 25 'stuck' closed valves were subjected to the detailed failure examinations. As will be described subsequently, a total 12 valves that did not open during the initial testing were subjected to the detailed failure examinations.

The examinations included observations of the conditions of the valves (visually and under a low power stereomicroscope), infrared analyses on the sealing gaskets to identify the materials from which they are made, Shore D hardness measurements on the gasket materials, and forensic analyses of the valves once disassembled. As the valves were being disassembled, the spring force versus deflection was measured and the spring characteristics were analyzed to determine whether changes, such as stress relaxation, occurred during service or whether the spring characteristics for PRVs from a given vendor are consistent.

The above examinations and measurements were made on 12 valves that were 'stuck' closed (did not open by 375 psig) in the original test program, 16 valves that exhibited high start-to-discharge pressures (greater than 110 percent of the set pressure), and 10 valves that exhibited low start-to-discharge pressures (less than the set pressure). In addition, six valves that were not tested during the previous study but were tested in the present study were visually examined and one was disassembled for more detailed examinations (PRV 407). A new valve (PRV 146) from Manufacturer A was also disassembled and examined to provide data for comparison of the spring force measurements and the gasket materials with the PRVs that had been removed from service.

Some of the valves that were disassembled in the initial performance testing program were also reexamined to see if additional data on the cause of their inadequate performance (according to the previously stated performance criteria) could be determined. These valves consisted of four that were 'stuck' shut, five with high start-to-discharge pressures, and four with low start-to-discharge pressures.

The PRVs selected for failure analysis are presented in Table 10 and the detailed results of the examinations are provided in Appendix A.

Table 10 – PRVs Selected for Failure Analysis

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[(a)]	INITIAL VISUAL INSPECTION
PRV ID	PRV Mfg ID	PRV Type[(b)]	PRV Size (in)	PRV Age (yrs)	Climate		
250-psi Set Point PRVs							
279	A	I	1	17	Cool, damp	DNO	Bugs and debris in valve body; valve body surfaces discolored; internal rain cap but no obvious rain cap line; weep hole open
350	B	I	1	22	Cool, damp	DNO	Internal rain cap; surfaces of valve body discolored –nearly black; valve body distorted (oval)
274	A	I	¾	43	Cool, damp	DNO	No rain cap; outside and inside surfaces of valve body painted silver; gasket holder painted silver; weep hole open
292	G	I	1	43	Cool, damp	DNO	No rain cap; gasket holder had a screw through the top; screw surfaces were corroded; internal surface was discolored; there was some loose debris in the valve body; the weep hole was open; the external surface was discolored and partially covered with blue paint

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[a]	INITIAL VISUAL INSPECTION
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**	**Climate**		
173	A	I	¾	**44**	Warm, damp	DNO	No rain cap; external surface of valve body had silver and white paint; weep hole plugged with paint; inside surfaces of valve body discolored
326	A	I	¾	**45**	Warm, damp	DNO	No rain cap; silver paint on inside and outside surfaces of valve body; weep hole plugged with paint; o-ring, painted silver on thread
250	A	I	1	**51**	Cool, damp	DNO	No rain cap; faint rain cap line on inside surface of valve body; debris (cob webs) inside valve body; internal surfaces discolored
102	A	I	1	**52**	Cool, damp	DNO	No rain cap; external surface of valve body painted light blue; dried mud, corrosion and debris inside valve body; weep hole open
62	Other (Roney)	E	¾	**57**	Warm, dry	DNO	No rain cap; heavy corrosion on spring inside the valve body; external surfaces of valve body had been buffed to read valve data
141	C	I	1	**5**	Warm, dry	High s-t-d	No rain cap; external surface of valve body had been buffed to read valve data; very little discoloration of the internal surfaces of the valve body; weep hole open
202	A	I	¾	**6**	Warm, damp	High s-t-d	No rain cap and no distinct rain cap line; blotchy discoloration on inside surface of valve body; no debris inside valve body
351	B	I	¾	**12**	Warm, dry	High s-t-d	No rain cap but distinct rain cap line on external surface of valve body; very little discoloration of inside surfaces of valve body and very little debris inside valve body; weep hole open

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[a]	INITIAL VISUAL INSPECTION
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**	**Climate**		
132	A	I	¾	**13**	Cool, dry	High s-t-d	No rain cap; rain cap line on external surface; very little discoloration on inside surfaces of valve body; weep hole open
281	A	I	1	**14**	Cool, damp	High s-t-d	No rain cap; external and internal surfaces of valve body somewhat discolored but no loose corrosion products
398	C	I	¾	**19**	Cool, dry	High s-t-d	No rain cap; rain cap line on external surface of valve body; external surface discolored; light corrosion and debris on inside surfaces of valve body; weep hole open
196	A	I	1	**24**	Cool, damp	High s-t-d	No rain cap; weep hole plugged with paint; external surfaces of valve body had been cleaned with a fine wire brush to read valve data; no debris or lose corrosion inside the valve body
283	A	I	1-¼	**28**	Cool, damp	High s-t-d	No rain cap
407	A	I	1	**32**	Cool, dry	High s-t-d	Internal rain cap; internal surfaces of valve body discolored, but no loose debris inside the valve body; weep hole open; white paint on external surface of valve body
359	B	I	¾	**35**	Warm, damp	High s-t-d	Rain cap not reported; external and internal surfaces discolored; some corrosion products on valve body surfaces; weep hole half plugged with corrosion products
343	B	I	¾	**42**	Cool, damp	High s-t-d	No rain cap; external and internal surfaces of valve body discolored but no loose corrosion products
270	D	I	1	**45**	Cool, damp	High s-t-d	No rain cap; no rain cap line; external surfaces of valve body painted silver; internal surfaces discolored; weep hole open; corrosion on spring

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[a]	INITIAL VISUAL INSPECTION
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**	**Climate**		
268	D	I	1	**52**	Cool, damp	High s-t-d	No rain cap; no rain cap line; inside surfaces of valve body discolored, but no loose debris in valve body; weep hole plugged with paint
251	A	I	1	**53**	Cool, damp	High s-t-d	No rain cap; no rain cap line; inside surfaces of valve body discolored but no debris in valve body; weep hole plugged with paint
262	A	I	1	**4**	Cool, damp	Low s-t-d	Rain cap; internal surfaces of valve body discolored; but no corrosion or loose debris in valve body; weep hole open
383	C	I	¾	**5**	Warm, dry	Low s-t-d	No rain cap but had a rain cap line; small amount of discoloration/corrosion on inside surface of valve body; weep hole open
468	C	I	¾	**8**	Cool, damp	Low s-t-d	Rain cap; inside surfaces of valve body not significantly discolored only a few small, dark stain spots; small amount of fuzzy debris inside valve body; weep hole open
211	C	I	1-¼	**11**	Cool, dry	Low s-t-d	Rain cap; internal and external surfaces of valve body discolored but no loose debris or corrosion products inside the valve body; weep hole open
349	A	I	1-¼	**15**	Cool, damp	Low s-t-d	No rain cap; internal surfaces of valve body discolored and small amount of debris inside valve body; weep hole open
329	A	I	¾	**36**	Warm, damp	Low s-t-d	No rain cap; no rain cap line; external surface of valve body discolored and partially covered with silver paint; external surface of valve body gouged, most likely with a pipe wrench; silver paint on inside surface of valve body; weep hole plugged with paint; some loose debris inside valve body

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[a]	INITIAL VISUAL INSPECTION
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**	**Climate**		
396	A	I	¾	**36**	Cool, dry	Low s-t-d	Internal rain cap; rain cap and external surfaces of valve body painted silver; some silver paint on inside surfaces of valve body; weep hole plugged with paint
443	F	I	1-¼	**6**	Cool, damp	Low s-t-d	No rain cap; external and internal surfaces of valve body discolored; no loose debris inside valve body; weep hole open
146	A	I	¾	**New**	New	Not pressure tested	New PRV
275-psi Set Point PRVs							
7	B	I	¾	**21**	Warm, dry	DNO	No rain cap; no rain cap line; external surfaces of valve body had been wire brushed to read valve data; slight discoloration of internal surfaces of the valve body; small amount of debris inside valve body; weep hole open
5	B	I	¾	**28**	Warm, dry	DNO	No rain cap; no rain cap line; external surfaces of valve body had been wire buffed to read valve data; some discoloration of inside surface of valve body; cobwebs inside valve body; weep hole open
80	B	E	¾	**36**	Warm, dry	DNO	No rain cap; external surfaces of valve body discolored; significant amount of debris, dirt and cobwebs inside the valve body; internal surfaces of the valve body were discolored but did not appear to be significantly corroded

PRV INFORMATION						ISSUE FROM ORIGINAL TEST[a]	INITIAL VISUAL INSPECTION
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**	**Climate**		
75	B	E	¾	**20**	Warm, dry	High s-t-d	No rain cap; cobwebs/dust in spring area inside the valve body; inside surfaces of valve body were not significantly discolored; external surface if valve body was partially covered with blue paint; weep hole was open
19	B	I	¾	**25**	Warm, dry	High s-t-d	No rain cap; faint rain-cap line; external and internal surfaces of valve body discolored; some aluminum paint spots on inside surface but very little debris inside the valve body; slight corrosion on valve stem near the gasket holder
41	A	I	1	**29**	Warm, dry	High s-t-d	No rain cap; corrosion on spring; paint build-up in threads of the valve body; external and internal surfaces of valve body were discolored, but no loose corrosion products were present
57	E	I	¾	**47**	Warm, dry	Low s-t-d	No rain cap; faint rain cap line external and internal surfaces of valve body discolored; small amount of loose debris inside the valve body; weep hole open; one leg of guide spacer was deformed
56	E	I	¾	**48**	Warm, dry	Low s-t-d	No rain cap; no rain cap line; external and internal surfaces of valve body were discolored; small amount of debris inside valve body; weep hole open

(a) DNO = did not open; s-t-d = start to discharge
(b) I = internal; E = external

4.1 PRV Spring Analyses

As part of the failure analysis the spring characteristics from the disassembled PRVs were evaluated to determine if there were common spring sizes and strengths (load-displacement characteristics), particularly for those springs used by specific PRV manufacturers. Although Battelle did not have access to the manufacturer's specifications for the springs, it was believed that measuring the spring sizes and displacement characteristics might indicate whether relaxation of the springs occurred during the service of the PRVs.

As the springs were examined visually, the length of the installed (compressed) spring was measured. When the PRVs were disassembled, the relaxed spring length, coil diameter, spring wire diameter, and the spring load-displacement characteristics were measured. The load-displacement characteristics were measured on an Instron universal testing machine.

After all these data were collected, springs with common manufacturers, spring wire diameter, coil diameters, and lengths were grouped together to determine if the load-displacement characteristics and the PRV spring loads were comparable or to determine if there was a decrease in the load-displacement values for common spring sizes with time in service. In at least one set of data springs of common sizes, but from different valve manufacturers were grouped together. The results of those measurements and evaluations are listed in Table 11.

In Table 11, the column labeled "Spring Displacement" is the difference between the installed spring length and the unloaded or relaxed spring length measured after the spring was unloaded. The column labeled "Spring Load-Displacement" is the measured load-displacement curve for the spring from the Instron machine. In all cases the load-displacement curves for the individual springs are linear. The column labeled "Spring Load" is calculated by multiplying the spring displacement by the spring load displacement. That value represents the load on the spring.

For the PRVs that were disassembled during the initial study conducted during 2009, the installed spring length was not measured; consequently, the Spring Displacement and the Spring Load could not be determined. Those valves and springs are indicated by the (b) in the appropriate columns in the table. However, the load-displacement curves for those springs were measured to provide data that may have indicated that spring relaxation had occurred. In addition, since all of the springs were not measured at the same time, it wasn't known if other valves with similar sized springs would be disassembled and analyzed. Thus in some instances there was only one spring of a certain size when all of the data were assembled for analysis and the data for those individual springs was not useful.

Table 11 – Spring Displacement and Load Data

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[a]	SPRING MEASUREMENTS		
PRV ID	PRV Mfg ID	PRV Type[c]	PRV Size (in)	PRV Age (yrs)		Spring Displacement (in)	Spring Load/ Displacement (lbs/in)	Spring Load (lbs)
250-psi Set Point PRVs								
Nominal Wire Diameter = 0.163"; Disassembled Spring Length = ~4.2"								
146	A	I	¾	**New**	None	0.549	242.0	132.9
396	A	I	¾	**36**	Low s-t-d	0.586	221.1	129.6

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[a]	SPRING MEASUREMENTS		
PRV ID	**PRV Mfg ID**	**PRV Type[c]**	**PRV Size (in)**	**PRV Age (yrs)**		**Spring Displacement (in)**	**Spring Load/ Displacement (lbs/in)**	**Spring Load (lbs)**
329	A	I	¾	**36**	Low s-t-d	0.655	222.2	145.5
202	A	I	¾	**6**	High s-t-d	0.653	220.3	143.8
132	A	I	¾	**13**	High s-t-d	0.560	232.0	129.9
274	A	I	¾	**43**	DNO	0.676	224.3	151.6
173	A	I	¾	**44**	DNO	0.748	218.0	163.1
326	A	I	¾	**45**	DNO	0.676	223.1	150.8
Nominal Wire Diameter = 0.127”; Disassembled Spring Length = ~2.9”								
281	A	I	1	**14**	High s-t-d	-[b]	130.3	-[b]
Nominal Wire Diameter =0.144”; Disassembled Spring Length = ~4.1”								
351	B	I	¾	**12**	High s-t-d	0.747	170.9	127.6
343	B	I	¾	**42**	High s-t-d	0.774	157.9	122.2
Nominal Wire Diameter = 0.163”; Disassembled Spring Length = ~5.1”								
383	C	I	¾	**5**	Low s-t-d	0.938	152.9	143.4
468	C	I	¾	**8**	Low s-t-d	-[b]	150.4	-[b]
398	C	I	¾	**19**	High s-t-d	0.867	159.6	138.4
Nominal Wire Diameter = 0.165”; Disassembled Spring Length = ~6.2”								
270	D	I	1	**45**	High s-t-d	1.132	162.5	183.9
268	D	I	1	**52**	High s-t-d	1.144	162.5	185.9
Nominal Wire Diameter = 0.172”; Disassembled Spring Length = ~6.1”								
251	A	I	1	**53**	High s-t-d	1.166	156.6	182.5
250	A	I	1	**51**	DNO	1.082	160.7	173.9
102	A	I	1	**52**	DNO	1.125	172.2	193.7
Nominal Wire Diameter = 0.187”; Disassembled Spring Length = ~4.5”								
279	A	I	1	**17**	DNO	-[b]	185.3	-[b]
350	B	I	1	**22**	DNO	1.136	199.9	227.0
196	A	I	1	**24**	High s-t-d	0.963	186.3	179.4
407	A	I	1	**32**	High s-t-d	1.061	190.9	202.6
262	A	I	1	**4**	Low s-t-d	-[b]	177.8	-[b]
Nominal Wire Diameter = 0.194”; Disassembled Spring Length = ~4.4”								
292	G	I	1	**43**	DNO	0.952	182.7	173.9

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[a]	SPRING MEASUREMENTS		
PRV ID	**PRV Mfg ID**	**PRV Type[c]**	**PRV Size (in)**	**PRV Age (yrs)**		**Spring Displacement (in)**	**Spring Load/ Displacement (lbs/in)**	**Spring Load (lbs)**
Disassembled Spring Length = ~7.0”								
141	C	I	1	**5**	High s-t-d	-[b]	191.2	-[b]
211	C	I	1-¼	**11**	Low s-t-d	-[b]	319.4	-[b]
Nominal Wire Diameter = 0.251”; Disassembled Spring Length = 4.8”								
349	A	I	1-¼	**15**	Low s-t-d	-[b]	364.1	-[b]
Nominal Wire Diameter = 0.252”; Disassembled Spring Length = ~6.0”								
443	F	I	1-¼	**6**	Low s-t-d	-[b]	281.2	-[b]
275-psi Set Point PRVs								
Nominal Wire Diameter = 0.140”; Disassembled Spring Length = ~2.7”								
75	B	E	¾	**20**	High s-t-d	-[b]	140.2	-[b]
80	B	E	¾	**36**	DNO	-[b]	147.2	-[b]
Nominal Wire Diameter = 0.146”; Disassembled Spring Length = ~4.0” to 4.2”								
7	B	I	¾	**21**	DNO	-[b]	158.5	-[b]
5	B	I	¾	**28**	DNO	-[b]	155.6	-[b]
19	B	I	¾	**25**	High s-t-d	-[b]	153.8	-[b]
Nominal Wire Diameter = 0.186”; Disassembled Spring Length = ~4.6”								
41	A	I	1	**29**	High s-t-d	-[b]	184.7	-[b]
Nominal Wire Diameter = 0.157”; Disassembled Spring Length = ~5.1”								
57	E	I	¾	**47**	Low s-t-d	0.945	156.5	147.9
56	E	I	¾	**48**	Low s-t-d	1.003	156.4	156.9

(a) DNO = did not open; s-t-d = start to discharge
(b) Disassembled during original test program conducted in 2009; installed spring length was not measured in these evaluations and therefore the data was not available.
(c) I = internal; E = external

Comparison of the data for the first eight springs listed in Table 11, all from Manufacturer A, shows that the spring load-displacement value was highest (242 lbs/in) for the new valve (PRV 146) and next highest (232 lbs/in) for PRV 132 which had been in service for 13 years. The load-displacement values for the remaining springs from PRVs that had been in service for times ranging from 28 to 45 years ranged from 218 to 224 lbs/in. That observation could indicate possible relaxation of the older springs with time in service. However, when the PRV spring load was calculated, the PRVs with the highest spring loads were those that had been in service for the longer periods of time. In those cases the amount of spring displacement also was the highest. This observation suggests that the older springs had lower load-displacement values as manufactured; consequently, they required higher displacements to achieve the required spring load to meet the desired PRV set pressure.

Comparison of the spring data for another group of common size springs; for example, the springs from PRVs 383, 398, 468, 56, and 57 showed there was no correlation between the PRV performance (high start-to-discharge or low start-to-discharge) and the load-displacement value or the PRV spring load. Similar statements can be made for the group of springs from PRVs 270, 268, 251, 250, and 102.

Although new springs of each size were not available to compare the load-displacement characteristics against the PRVs pulled from service to assess possible stress relaxation, the calculated PRV spring loads were plotted versus the age of the PRVs in Figure 6 and spring loads versus the PRV age and manufacturer in Figure 7. The numbers next to the symbols in the chart represent the PRV identification number. Only the valves for which the spring force could be calculated are included in Figure 6 and Figure 7.

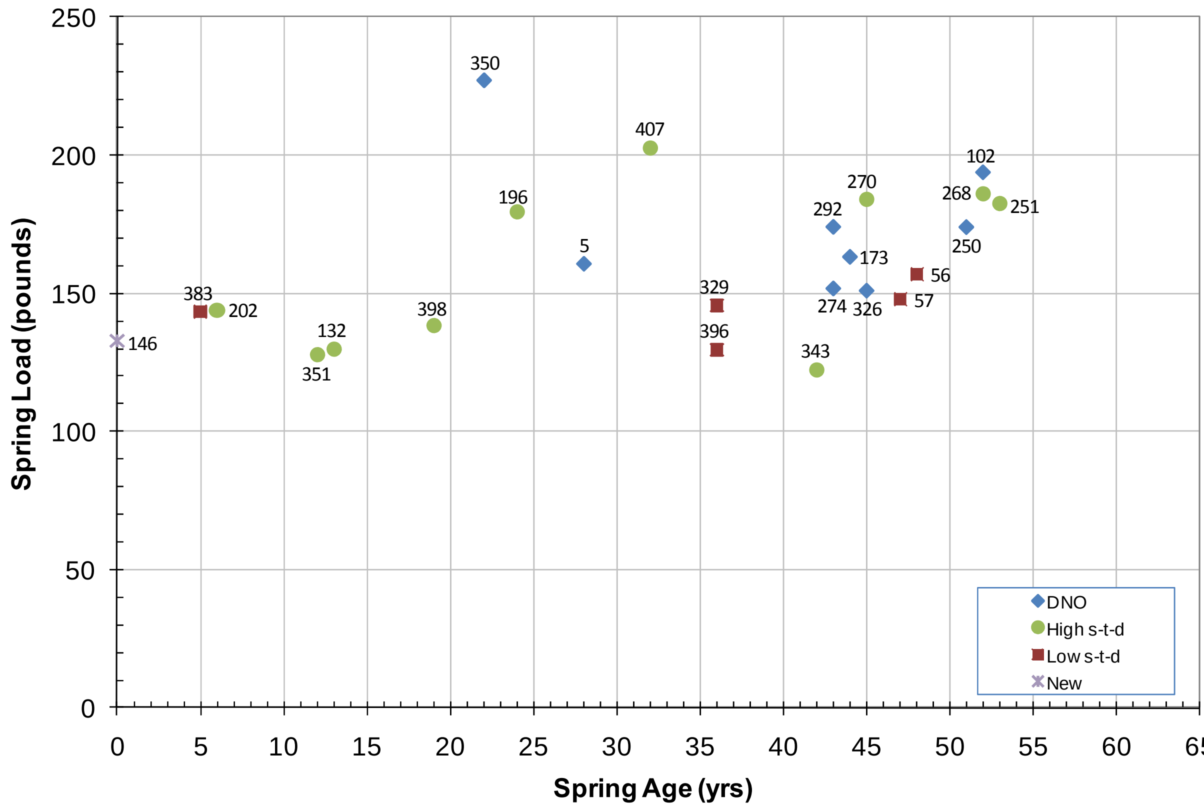

Figure 6 – PRV Spring Load versus Age

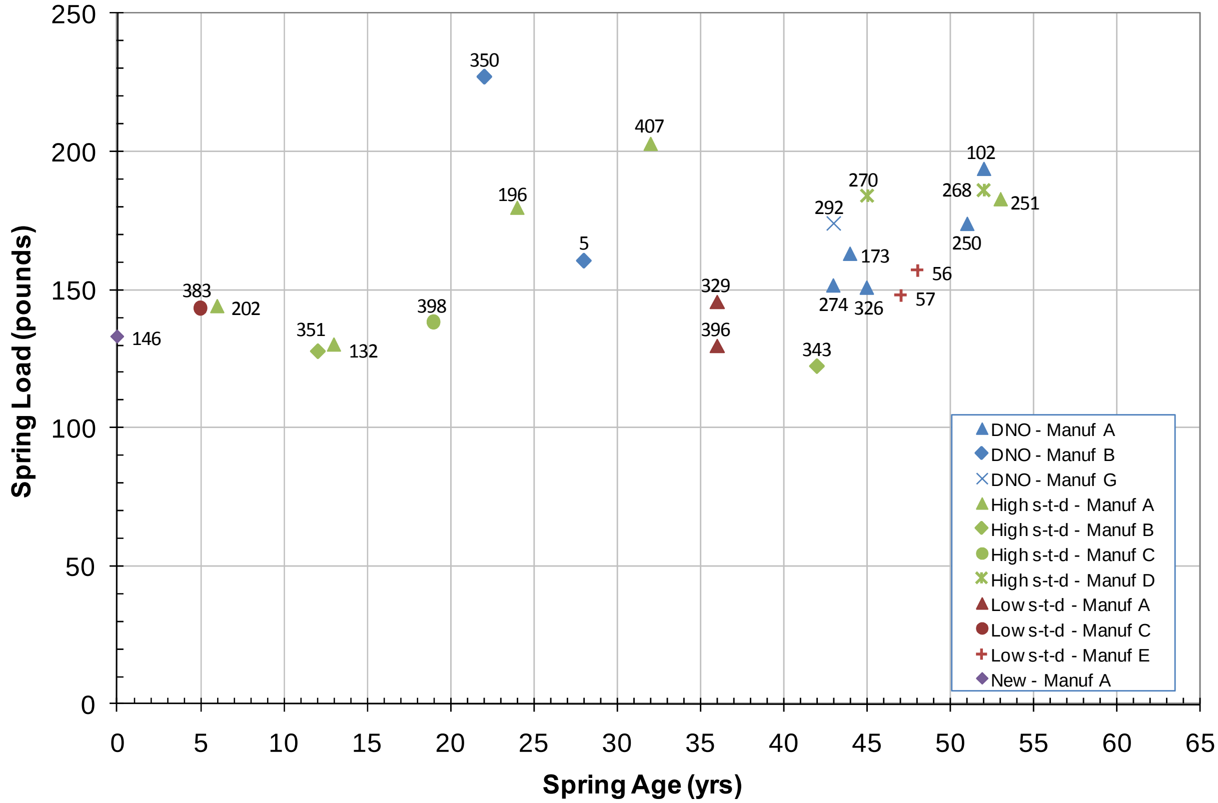

Figure 7 – PRV Spring Load versus Age and Manufacturer

Figure 6 and Figure 7 do not indicate a loss in PRV spring load as a function of time in service. Thus the spring analyses from the various PRVs evaluated does not indicate that stress relaxation (load loss) contributed to the deterioration in PRV performance (did not open, high start-to-discharge, or low start-to-discharge) when pressure tested. Figure 7 does indicate that spring loads for the PRVs from Manufacturers A, B, and C that were less than 20 years old ranged between about 130 and 145 pounds, whereas for the PRVs that were greater than 20 years old, the spring loads had greater variation between 125 and 227 pounds. In addition, all of the PRVs that did not open during the initial test program had spring loads of 150 pounds or greater. Unfortunately, many variables related to the valve and spring sizes will influence the spring load and those variables may account for the greater scatter in the older PRVs. Since the manufacturing specifications for the springs and the PRVs produced at different times were not available for review, it cannot be concluded that the differences observed reflect changes in design requirements or spring manufacturing procedures.

As shown in Figure 6 and Figure 7, there was one PRV (PRV 350) that had a higher spring load, 227 pounds, than the others. That spring also exhibited the highest load-displacement value and had the largest installed spring displacement for the group of comparably sized springs. The area of the gasket from this PRV that would be exposed to the propane tank pressure was calculated to be 0.72 in^2. With the PRV spring load of 227 pounds, the calculated pressure required to open the valve (overcome the spring load) would be approximately 315 psig. Thus, the high spring load for PRV 350 was caused by a spring with a higher load-displacement value and a greater installed displacement, i.e. the PRV pressure set point likely was set high.

4.2 Seat Disc (Gasket) Material Analyses

When some of the PRVs tested during the initial study in 2009 were inspected, it was noted that in three of the four valves that did not open at 375 psig, the gasket was stuck to the valve body. The gasket in the fourth PRV was not disassembled and examined. In addition, it was found that the gasket in PRV 211, which opened immediately during testing, was separated into two pieces. Thus gasket issues could be a significant contributor to poor PRV performance.

In the present study the gaskets from the PRVs selected were examined to 1) assess their overall appearance after being in service, 2) determine the rubber or polymer material from which the gaskets were made, and 3) measure the hardness of the gasket material. In addition, if the gasket stuck to the valve body when the PRV was disassembled, the load required to break the seal was measured by pushing on the valve stem in an Instron universal testing machine.

The overall condition of the gaskets was assessed by visual examination and under a low power stereomicroscope. The gasket material identification was determined using Fourier-Transform-Infrared (FT-IR) Spectroscopy. In addition, the hardness of the gaskets was measured using the Shore D scale.

When the 38 PRVs were disassembled for detailed examinations, the gasket stuck to the valve body in five of the PRVs. Those PRVs and the loads and displacements required to break the seal are listed in Table 12.

Table 12 – Loads and Displacements to Dislodge Gaskets from the Valve Bodies after PRV Disassembly

PRV ID	PRV Age (yrs)	PRV Set Pressure (psig)	Load (lbs)	Displacement (in)[10]
173	**44**	250	20.1	0.022
274	**43**	250	56.9	0.016
5	**28**	275	31.6	0.011
250	**51**	250	115.6	0.023
292	**43**	250	135.9	0.005

As shown in Table 12, the loads required to loosen the gaskets from the valve bodies ranged from about 20 to 136 pounds and the displacements ranged from 0.005 to 0.023 inch. The measured displacements show that these gaskets exhibited some elasticity. Considering the area of the gasket and the load to dislodge the gasket, the equivalent estimated start-to-discharge pressures for these PRVs are estimated to be 208 psig or lower. Yet the set pressure for all of the PRVs in Table 12 was either 250-psig or 275-psig. Consequently, if the gasket was the only factor contributing to the PRV performance issues, the test pressures used in the initial study

[10] The values in the displacement column represent the distance on the X-axis of the load displacement curve before the load dropped indicating that the gasket was free. The gaskets showed some elastic behavior before they broke loose.

should have unstuck the gaskets. As such, the data indicate stuck gaskets may contribute to, but are not the main cause of the failure of the PRVs to open at their set pressures. However, it has been suggested that the spring force and the gasket-stuck force may be additive. In other words they are similar to two springs in series. Experiments would need to be designed and conducted to resolve this issue and is outside the scope of this analysis.

The results of the FTIR spectroscopy analysis and the Shore D hardness measurements on the gaskets are presented in Table 13. As is shown in the table, the gaskets in all but two of the PRVs were made from Buna N or modified Buna N. In some cases, a filler material was also identified. The gaskets from the other two PRVs examined were made from Viton.

Table 13 – PRV Gasket Material Data

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[(a)]	POLYMER MEASUREMENTS			
PRV ID	**PRV Mfg ID**	**PRV Type[(b)]**	**PRV Size (in)**	**PRV Age (yrs)**		**Polymer Type**	**Trade Name**	**Shore D Hardness**	**Notes**
250-psi Set Point PRVs									
279	A	I	1	**17**	DNO	Butadiene-acrylonitrile copolymer	Buna N	40	Compression set rings, radial cracks in outer circumferential ring, loose in holder
350	B	I	1	**22**	DNO	Butadiene-acrylonitrile copolymer; Mg carbonate filler	Buna N	22	Compression set rings indicate seal was off center, no cracks, removed from holder easily
274	A	I	¾	**43**	DNO	Butadiene-acrylonitrile copolymer	Buna N	48	Compression set rings, stuck in holder, broke into many pieces when pulled on to remove
292	G	I	1	**43**	DNO	(c)		63	Compression set rings, no cracks, difficult to remove from the holder
173	A	I	¾	**44**	DNO	Butadiene acrylonitrile copolymer	Buna N	51	Compression set rings, radial cracks in outer circumferential ring, stuck in holder, broke into many pieces when pulled on to remove
326	A	I	¾	**45**	DNO	Butadiene-acrylonitrile copolymer	Buna N	58	Compression set rings, stuck in holder, broke into several pieces when pulled on to remove
250	A	I	1	**51**	DNO	(c)		38	Compression set rings
102	A	I	1	**52**	DNO	Butadiene-acrylonitrile copolymer	Buna N	30	Compression set rings, no cracks, removed from holder easily
141	C	I	1	**5**	High s-t-d	Possible terpolymer with butadiene-acrylonitrile; possible inorganic sulfate filler	XBNR or HBNR type of Buna N	38	Compression set rings, no cracks, loose in holder and easily removed

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[(a)]	POLYMER MEASUREMENTS			
PRV ID	**PRV Mfg ID**	**PRV Type[(b)]**	**PRV Size (in)**	**PRV Age (yrs)**		**Polymer Type**	**Trade Name**	**Shore D Hardness**	**Notes**
202	A	I	¾	**6**	High s-t-d	Butadiene-acrylonitrile copolymer	Buna N	36	Compression set rings, no cracks, loose in holder
351	B	I	¾	**12**	High s-t-d	Butadiene-acrylonitrile copolymer; Mg carbonate filler, possible Mg silicate or clay filler	Buna N	28	Compression set rings
132	A	I	¾	**13**	High s-t-d	Butadiene-acrylonitrile copolymer	Buna N	51	Compression set rings, no cracks, stuck in holder, broke into several pieces when pulled on to remove
281	A	I	1	**14**	High s-t-d	Butadiene-acrylonitrile copolymer; silicate filler	Buna N	34	Compression set rings indicate seal was off center, no cracks
398	C	I	¾	**19**	High s-t-d	Butadiene-acrylonitrile copolymer; Ester functionality present, possible inorganic sulfate filler	Buna N	36	Compression set rings
196	A	I	1	**24**	High s-t-d	Polybutadiene; weak spectrum; possible acrylonitrile copolymer	PBD Buna N?	35	Compression set rings, no cracks, gasket loose in holder, easily removed, gasket pliable
283	A	I	1-¼	**28**	High s-t-d	Butadiene-acrylonitrile copolymer, weak spectrum	Buna N	47	Compression set rings, no cracks, appeared stuck in holder but was removed easily
407	A	I	1	**32**	High s-t-d	(c)		35	Compression set rings, radial cracks in the outer circumferential ring, gasket was stiff and it cracked when it was removed
359	B	I	¾	**35**	High s-t-d	Butadiene-acrylonitrile copolymer; Mg carbonate filler	Buna N	24	Compression set rings

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[(a)]	POLYMER MEASUREMENTS			
PRV ID	**PRV Mfg ID**	**PRV Type[(b)]**	**PRV Size (in)**	**PRV Age (yrs)**		**Polymer Type**	**Trade Name**	**Shore D Hardness**	**Notes**
343	B	I	¾	**42**	High s-t-d	Butadiene-acrylonitrile copolymer; Mg carbonate filler	Buna N	21	Compression set rings, “alligator skin” appearance in the outer circumferential ring
270	D	I	1	**45**	High s-t-d	Butadiene-acrylonitrile copolymer	Buna N	38	Compression set rings, radial and circumferential cracks in the outer circumferential ring beyond the seal ring
268	D	I	1	**52**	High s-t-d	Butadiene-acrylonitrile copolymer	Buna N	38	Compression set rings, gasket discolored “alligator skin” appearance in the surface of the outer circumferential ring, loose in holder
251	A	I	1	**53**	High s-t-d	(c)		38	Compression set rings
262	A	I	1	**4**	Low s-t-d	Butadiene-acrylonitrile copolymer	Buna N	38	Compression set rings, gasket cracked
383	C	I	¾	**5**	Low s-t-d	Possible terpolymer with butadiene-acrylonitrile; Ester functionality present; possible inorganic sulfate	XBNR type of Buna N	33	Compression set rings, no cracks, gasket loose in holder and easily removed, gasket was pliable
468	C	I	¾	**8**	Low s-t-d	Butadiene-acrylonitrile copolymer Ester functionality present, possible inorganic sulfate filler	Buna N	21	Compression set rings, no cracks
427	F	I	1-¼	**10**	Low s-t-d	Vinylidene fluoride-hexafluoropropylene copolymer	Viton	23	Compression set rings

PRV INFORMATION					ISSUE FROM ORIGINAL TEST(a)	POLYMER MEASUREMENTS			
PRV ID	**PRV Mfg ID**	**PRV Type(b)**	**PRV Size (in)**	**PRV Age (yrs)**		**Polymer Type**	**Trade Name**	**Shore D Hardness**	**Notes**
211	C	I	1-¼	**11**	Low s-t-d	Possible terpolymer with butadiene-acrylonitrile; Ester functionality present, possible inorganic sulfate filler	XBNR or HBNR Type of Buna N	41	Compression set rings, gasket was in two pieces when valve was disassembled, circumferential cracks extended along the compression set ring, body seal surface edge may have cut the casket.
349	A	I	1-¼	**15**	Low s-t-d	Butadiene-acrylonitrile copolymer	Buna N	44	Compression set rings, no cracks
329	A	I	¾	**36**	Low s-t-d	Butadiene-acrylonitrile copolymer	Buna N	53	Compression set rings, gasket stuck in holder, casket cracked and fragments broke off when it was pulled on to remove it from the holder
396	A	I	¾	**36**	Low s-t-d	(c)		20	Compression set rings, radial cracks in outer circumferential ring, gasket easily removed, gasket was pliable
146	A	I	¾	**New**	None	Butadiene-acrylonitrile copolymer	Buna N	31	Compression set rings, no cracks
443	F	I	1-¼	**6**	Low s-t-d	Vinylidene fluoride-hexafluoropropylene copolymer	Viton	17	Compression set rings, no cracks, gasket loose in holder, easily removed
275-psi Set Point PRVs									
7	B	I	¾	**21**	DNO	Butadiene-acrylonitrile copolymer; Mg Carbonate filler	Buna N	24	Compression set rings indicate seal was off center, no cracks, loose in holder
5	B	I	¾	**28**	DNO	(c)		24	Compression set rings somewhat off center, no cracks, gasket was loose in holder and removed easily

PRV INFORMATION					ISSUE FROM ORIGINAL TEST[a]	POLYMER MEASUREMENTS			
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**		**Polymer Type**	**Trade Name**	**Shore D Hardness**	**Notes**
80	B	E	¾	**36**	DNO	Butadiene-acrylonitrile copolymer Mg carbonate filler	Buna N	24	Compression set rings, no cracks, gasket stuck in holder
75	B	E	¾	**20**	High s-t-d	(c)		33	Compression set rings, central region of gasket had a dull appearance, no cracks, gasket was pliable
19	B	I	¾	**25**	High s-t-d	Butadiene-acrylonitrile copolymer; Mg carbonate filler	Buna N	31	Compression set rings, no cracks, loose in holder
41	A	I	1	**29**	High s-t-d	Butadiene-acrylonitrile copolymer	Buna N	45	Compression set rings, no cracks
57	E	I	¾	**47**	Low s-t-d	Butadiene-acrylonitrile copolymer	Buna N	34	Compression set rings, gasket stuck in holder, difficult to remove, some gasket material transferred on washer
56	E	I	¾	**48**	Low s-t-d	Butadiene-acrylonitrile copolymer	Buna N	43	Compression set rings, gasket stuck in holder, difficult to remove, no cracks, some gasket material stuck to washer

(a) DNO = did not open; s-t-d = start to discharge
(b) I = internal; E = external
(c) IR analyses were not conducted, but based on other gasket data from the same PRV manufacturer these gaskets are most likely butadiene-acrylonitrile copolymers (Buna N).

It must be kept in mind that rubber formulations that are classified as Buna N can vary considerably based upon the manufacturers' formulations. They use different fillers and plasticizers to adjust the properties. Hence, the hardness can vary considerably from 6 to 58 using the Shore D scale. The hardness of the gaskets evaluated in this study range from 17 to 58 Shore D. However, the original hardnesses of the gaskets when they were produced were not known; thus estimates of how gasket hardness may have changed over time could not be made. The hardness of the gasket from PRV 146, which was a newly purchased valve that had never been in service, was 31 Shore D. The hardness of gaskets from other PRVs produced by the same manufacturer (Manufacturer A) ranged from 30 to 58 Shore D. The gasket with a hardness of 30 Shore D was in service for 52 years and the gasket with a hardness of 58 Shore D had been in service for 45 years. Consequently, there was not conclusive evidence that age affected the hardness of the gasket material.

The hardness of all the gaskets by performance issue (did not open, high s-t-d, low s-t-d) was plotted versus their age to see if there were general trends in their behavior over time (see Figure 8). The data shows no strong trends or correlations.

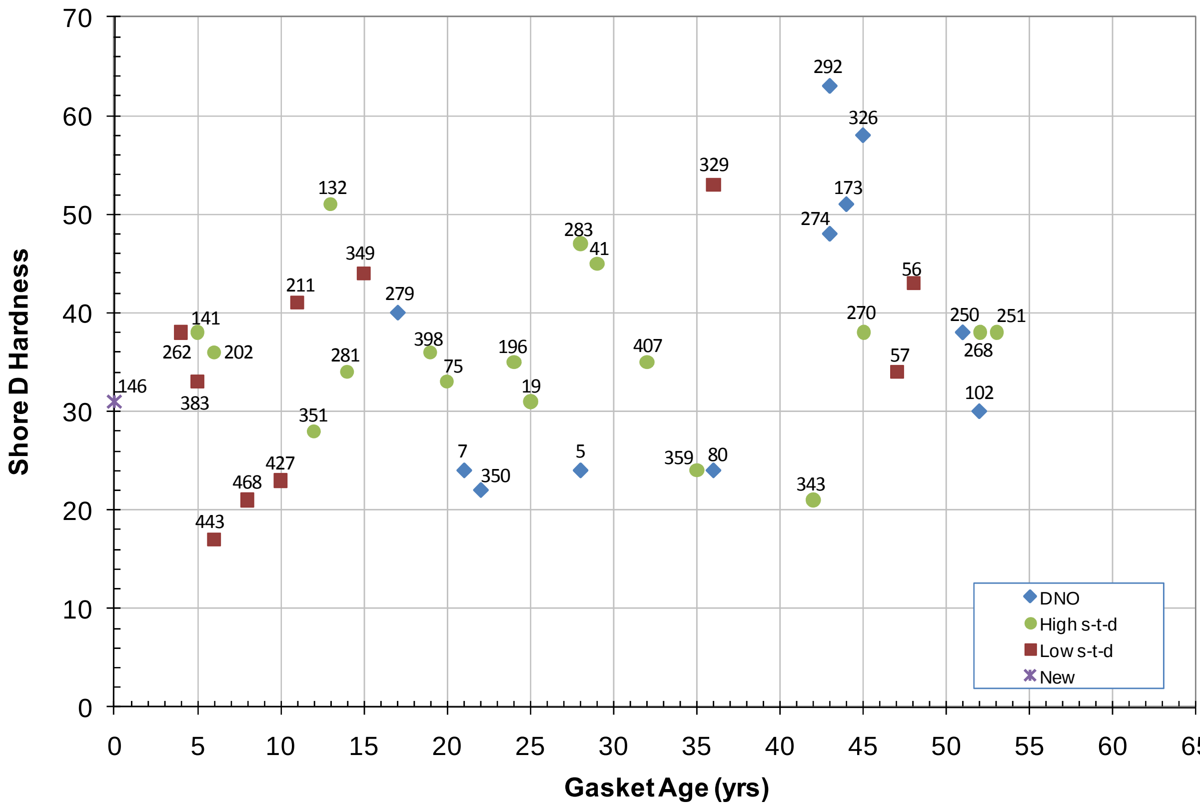

Figure 8 – Gasket Hardness versus Age

The results of the gasket examinations are also presented in Table 13. All of the gaskets exhibited compression set rings (see Figure 9), as would be expected. The compression set rings were somewhat off-center on the gaskets from PRVs 350 (DNO), 281 (high s-t-d), 7 (DNO), and 5 (DNO). As indicated, three of these PRVs did not open in the original test program and one exhibited a high start-to-discharge pressure. It is possible that this condition indicates possible misalignment of the valve stem/poppet in the PRV which could have contributed to their performance issues during testing. As will be illustrated subsequently, misalignment of the valve stem could result in a strong interaction between the valve stem surface and the guide spacer inner surface which could increase the load required to open the valve. Also moisture condensation in those regions could promote crevice corrosion which again could contribute to higher valve opening loads.

Figure 9 - Compression Set Rings on the Active/Sealing Surface of the Gasket From PRV 7
Note that the compression set rings are somewhat off center.

As is shown in Figure 10, the gasket from PRV 211 had been separated into two pieces. The primary crack followed a circumferential compression set ring and extended along that ring beyond where the gasket tore off, as is shown in Figure 10 through Figure 12. It is possible that the sealing surface edge in the valve body or the washer cut into the gasket. However, the reason why the gasket separated during service could not be identified.

The other features that indicate some deterioration of the gaskets during service were regions of material breaking off the outer edge of the gasket, radial and circumferential cracks in the outer circumferential ring (beyond the gasket seal region), roughened ‘alligator skin’ surface features, fragmenting of the gasket during removal, and finally regions of pull out from the seal surfaces and gasket material transfer to the valve body seal surfaces. All of these features are illustrated in Figure 13 through Figure 24. Except for the latter conditions, the deterioration was located beyond the seal area region and should not have had an effect on the performance of the PRVs. The material pull out and material transfer issue may contribute toward sticking but the equivalent pressures to overcome that condition were less than the PRV set pressures and obviously less than the maximum test pressure of 375 psig.

The only condition identified during the examination of the gasket material that conclusively resulted in the recorded PRV performance was the broken gasket in PRV 211 (discharged immediately when tested). That condition also was identified in the original PRV performance testing report [19]. It should be noted that the data sheet that accompanied PRV 211 did not indicate that the valve was removed because it was leaking.

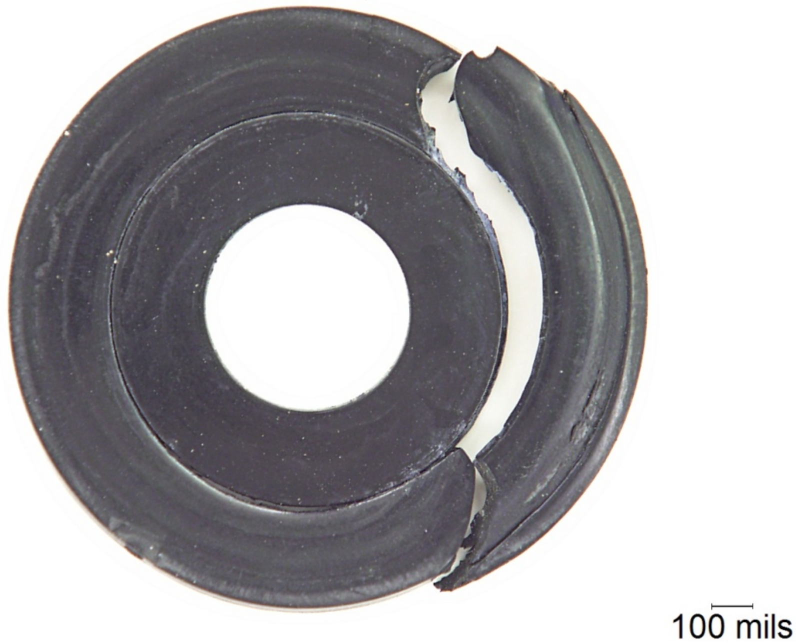

Figure 10 - Broken Gasket from PRV 211
The gasket was in two pieces when the PRV was disassembled.

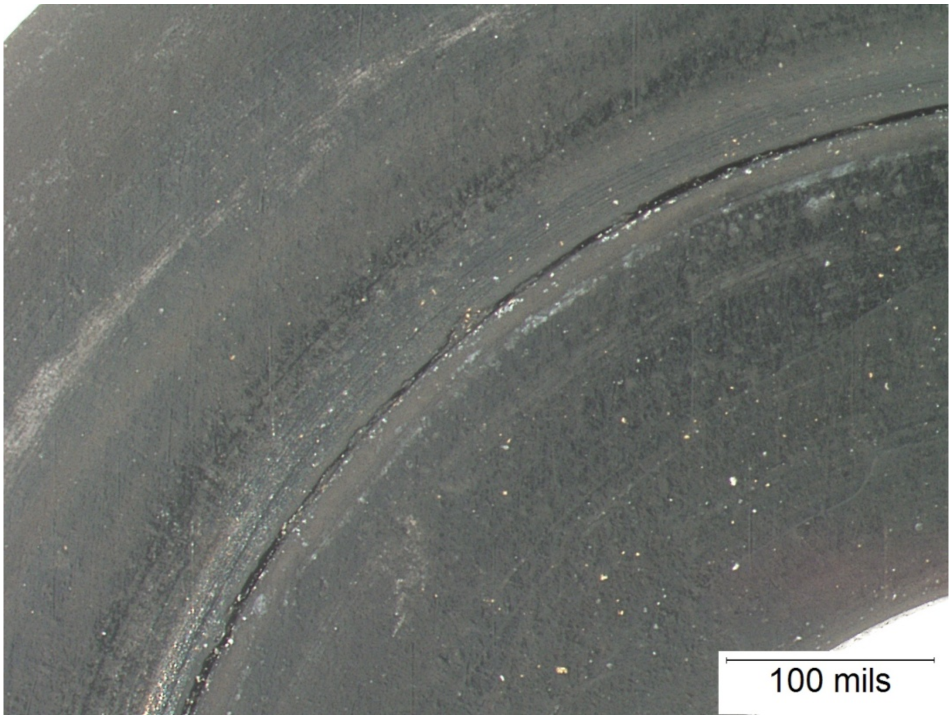

Figure 11 - Circumferential Crack Extending along the Compression Set Ring in the Gasket from PRV 211

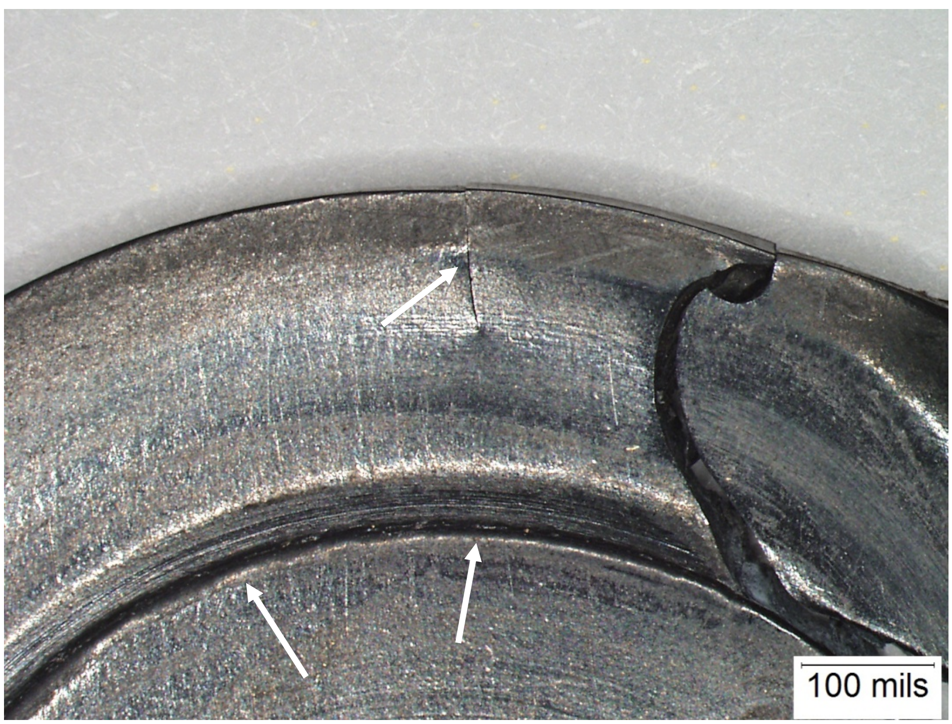

Figure 12 - Circumferential and Radial Cracks in the Gasket from PRV 211

Figure 13 - Sealing Surface of the Gasket from PRV 270
Note the smaller region where material had broken out (arrow). The gasket is still in the holder.

Figure 14 - Radial cracks in the Outer Circumferential Ring (Beyond the Seal Ring Surface) in the Gasket from PRV 270

Figure 15 – Higher Magnification View of Radial and Circumferential Cracks in the Surface of the Outer Circumferential Ring in PRV 270

Figure 16 - Radial Cracks in the Outer Circumferential Ring on the Sealing surface of the Gasket from PRV 329
The gasket is still in the holder

Figure 17 - Sealing Surface of the Gasket from PRV 343
Note the roughened surface in the outer circumferential ring and the compression set rings are somewhat off center; the latter condition perhaps indicating misalignment.

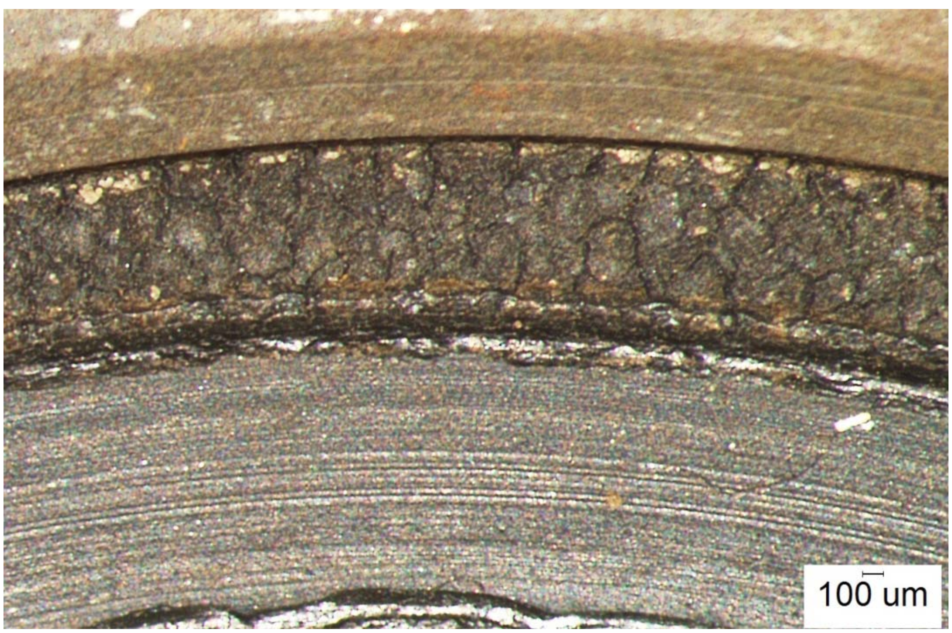

Figure 18 - Higher Magnification View of the Gasket Surface in the Outer Ring showing "Alligator Skin" Appearance of the Roughened Surface Region from PRV 343

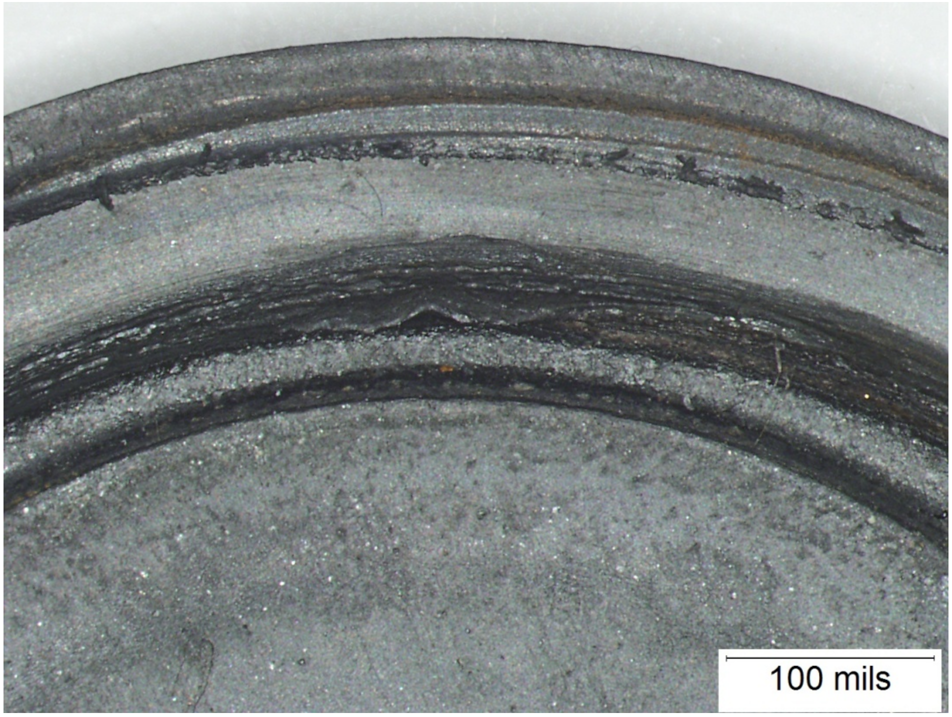

Figure 19 - Material Pull-Out Region on the Sealing Surface of the Gasket from PRV 350

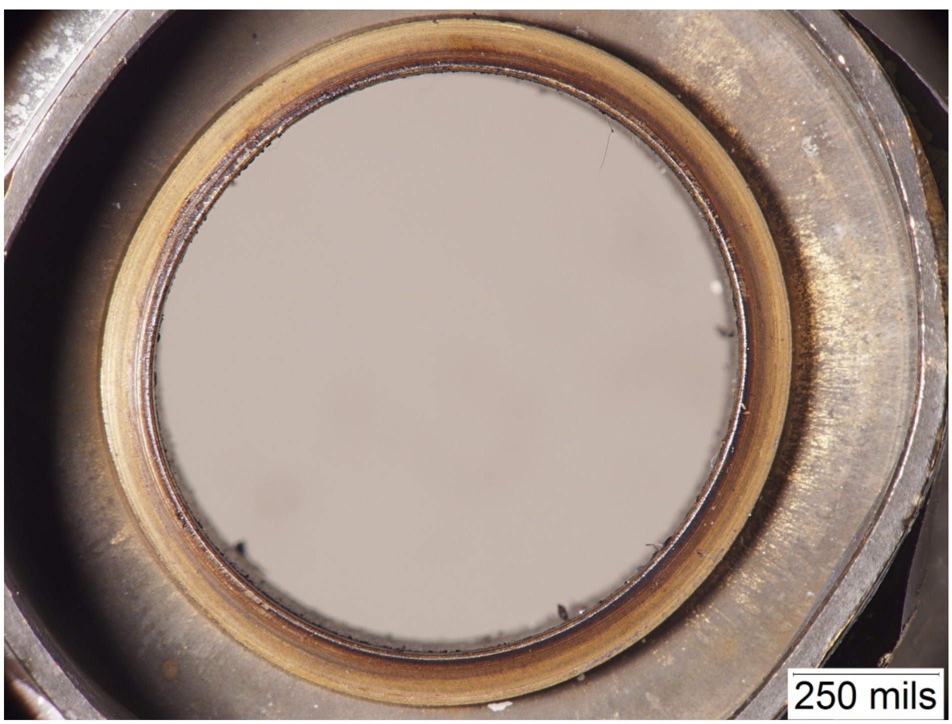

Figure 20 - Gasket Material Transferred on the Sealing Surface of the Valve Body from PRV 350

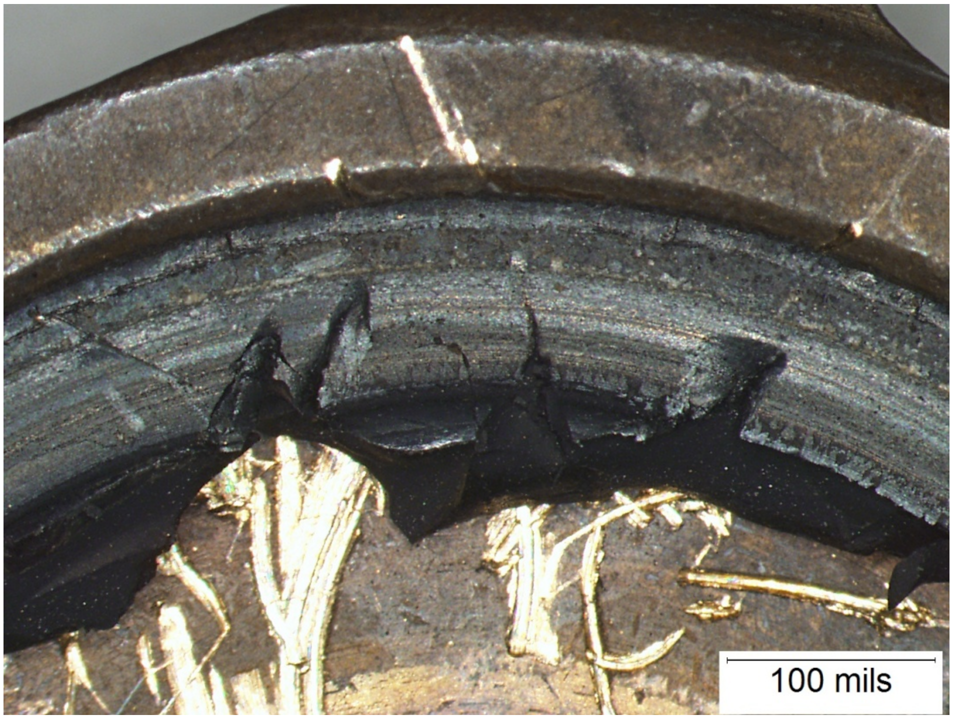

Figure 21 - Portion of the Gasket from PRV 273 Remaining in the Holder of PRV 273
This gasket tore into many small pieces when pulled on when trying to remove it from the holder.

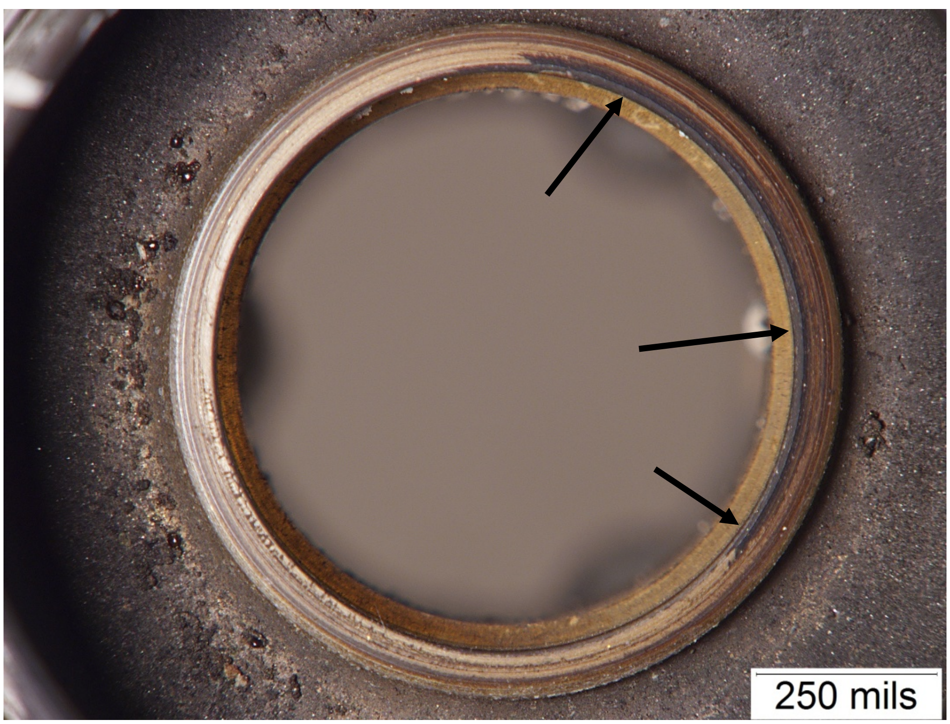

Figure 22 - Gasket Material (Arrows) Transferred to the Seal Surface on the Valve Body from PRV 273

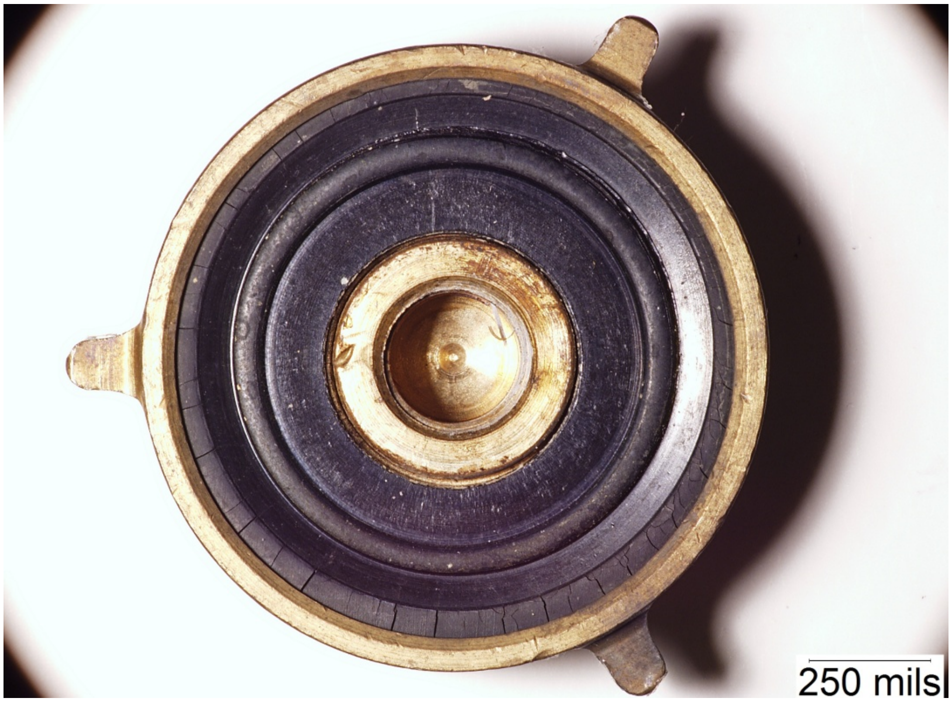

Figure 23 - Radial Cracks in the Outer Circumferential Ring (Beyond the Seal Region) in the Gasket from PRV 407

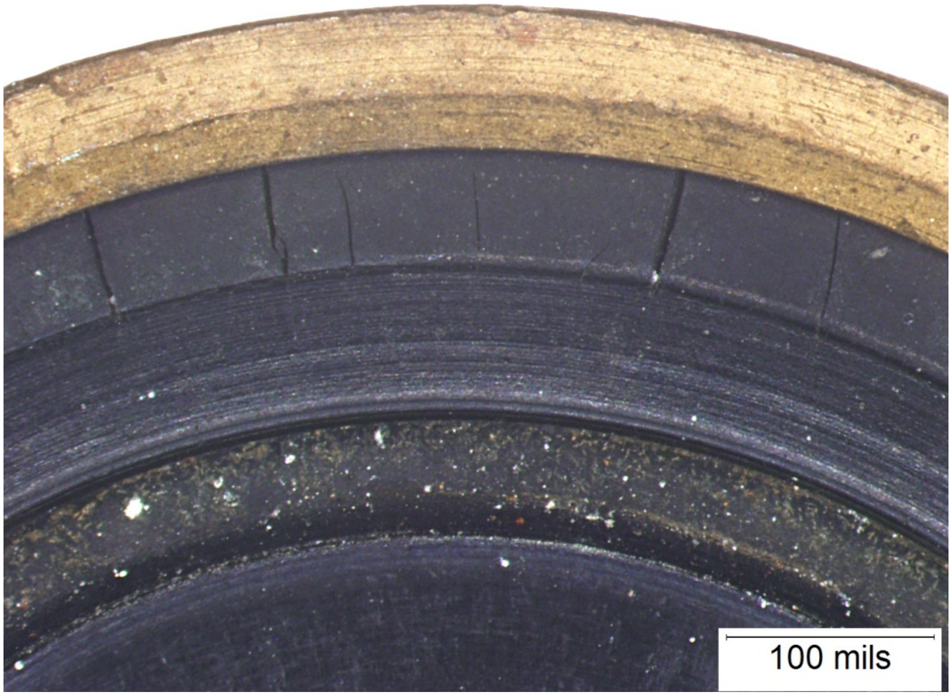

Figure 24 - Higher Magnification View of the Radial Cracks in the Gasket from PRV 407

4.3 Rain Cap Issues

When the pressure relief valves selected for examination were examined visually, it was observed that only 10 of 43 valves had rain caps included with the valve. This same observation was made during the initial study that most of the valves provided for testing did not have rain caps included. Also, many of the valves showed discoloration of the external and internal surfaces of the valve body, corrosion, and debris in the valve bodies. During discussions with PERC representatives, Battelle was asked to examine the valve bodies for evidence of either an external or internal rain cap line that would indicate if a rain cap had been present and possibly just not included with the valve when shipped for the performance testing program. Consequently during the follow-up analyses, the PRVs were examined for evidence that a rain cap had been present.

The results of the examination of the valves for further evidence that a rain cap had been present are summarized in Table 14.

Table 14 – Internal PRVs Rain Cap and Rain Cap Line Data

PRV ID	PRV Age (yrs	ISSUE FROM ORIGINAL TEST[a]	RAIN CAP PRESENT? YES/NO	RAIN CAP LINE PRESENT? YES/NO
54	Unk	DNO	No	Yes, but valve body surface was discolored
262	4	Low s-t-d	Yes	Yes
141	5	High s-t-d	No	External surface of valve body had been buffed
383	5	Low s-t-d	No	Yes
416	5	Low s-t-d	Yes	Yes
202	6	High s-t-d	No	Yes
443	6	Low s-t-d	No	Yes
418	7	Low s-t-d	No	Yes
468	8	Low s-t-d	Yes	Yes
484	10	OK	No	Yes
211	11	Low s-t-d	Yes	Not distinct, surface of valve body discolored
351	12	High s-t-d	No	Yes
132	13	High s-t-d	No	Yes
304	13	High s-t-d	Yes	Internal rain cap
281	14	High s-t-d	No	No
349	15	Low s-t-d	Yes	No
279	17	DNO	Yes	No
49	17	OK	No	Yes, valve body surface discolored
398	19	High s-t-d	No	Yes
120	20	DNO	No	No
7	21	DNO	No	No
350	22	DNO	Yes	Yes
196	24	High s-t-d	No	External surface of housing had been buffed
19	25	High s-t-d	No	Yes, faint
5	28	DNO	No	External surface of valve body had been buffed
208	28	OK	No	Yes, internal valve body surface discolored
41	29	High s-t-d	No	Possible internal rain cap
394	30	High s-t-d	Yes	Internal rain cap
407	32	High s-t-d	Yes	Internal rain cap

PRV ID	PRV Age (yrs	ISSUE FROM ORIGINAL TEST[(a)]	RAIN CAP PRESENT? YES/NO	RAIN CAP LINE PRESENT? YES/NO
329	**36**	Low s-t-d	No	No
396	**36**	Low s-t-d	Yes	Yes, internal rain cap
343	**42**	High s-t-d	No	Yes, but valve body surface was discolored
274	**43**	DNO	Yes	Yes, internal
292	**43**	DNO	No	Yes, valve body surface discolored
173	**44**	DNO	No	No
326	**45**	DNO	No	No
270	**45**	High s-t-d	No	No
57	**47**	Low s-t-d	No	Yes, but valve body surface discolored
64	**48**	DNO	No	No
56	**48**	Low s-t-d	No	No
250	**51**	DNO	No	No
102	**52**	DNO	No	No
268	**52**	High s-t-d	No	No
251	**53**	High s-t-d	No	No

(a) DNO – did not open; s-t-d –start-to-discharge; OK - open within set pressure tolerance

The results show that 25 of the 43 valves examined had evidence of a rain cap line. In some cases the rain cap line was very distinct, as is shown in Figure 26, in which the external rain cap line (protected area free from discoloration) on the external surface of the valve body from PRV 351 is quite evident. Although less evident, Figure 27 also shows a rain cap line in which the external surface of PRV 343 is discolored where the rain cap was affixed. Figure 28 shows the absence of a rain cap line on the external surface of the valve body from PRV 120; an internal rain cap line also was not visible on this valve.

In some instances the external surface of the valve body had been wire brushed or buffed to remove the oxide films to read the valve data and, as a result, it could not be determined whether a rain cap had been present. That condition on PRV 5 is illustrated in Figure 29.

Figure 30 shows a faint rain cap line on the internal surface of the valve body from PRV 350. This PRV had an internal rain plug as is shown in Figure 31. Several other PRVs had very faint internal rain cap lines.

This portion of the study has shown that about 60-percent of the PRVs that were studied had evidence of a rain cap being present even though none was included with the valve provided for study. For the 40-percent of PRVs without evidence of a rain cap being present, eight of these PRVs did not open in the original test program and only one met the UL 132 performance criteria for new valves (see Figure 25). The Battelle investigators strongly suggest that more attention to the presence of rain caps be given by tank users and tank service personnel. Keeping a rain cap in place should minimize debris from entering the valve.

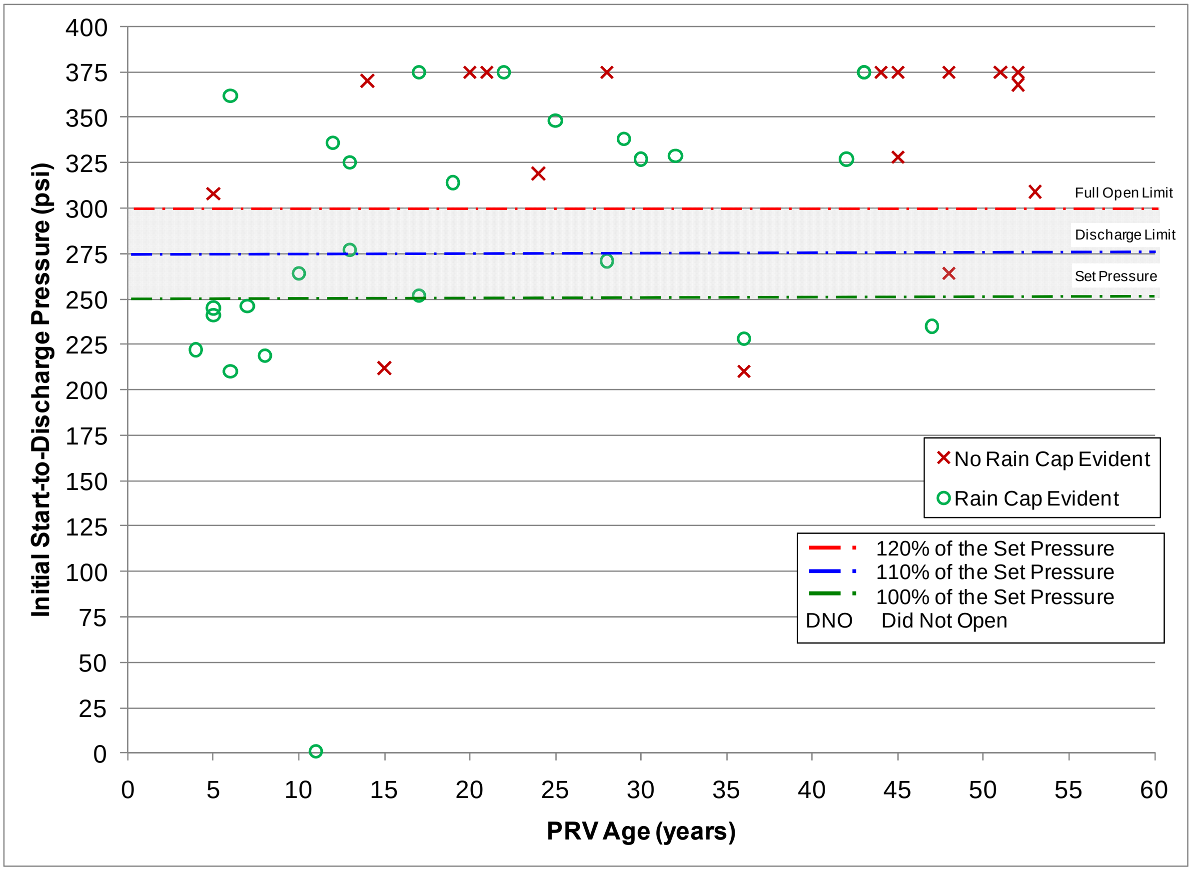

Figure 25 – Comparison of PRV Performance by PRVs with Evidence of a Rain Cap Line vs. PRVs without Evidence of a Rain Cap Line

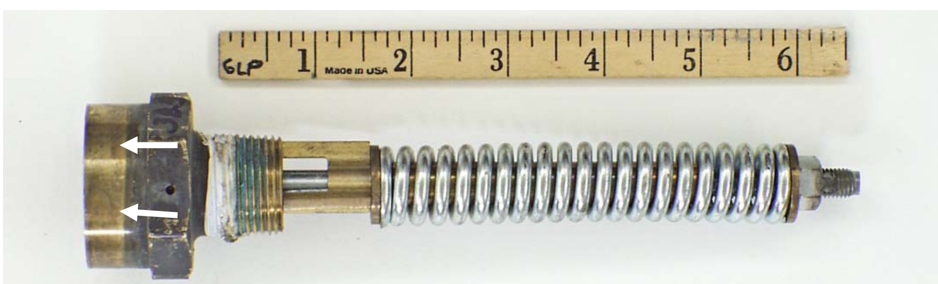

Figure 26 - Distinct Rain Cap Line on PRV 351

Figure 27 - Discolored External Surface of Valve Body under Rain Cap Line on PRV 343

Figure 28 - Absence of Rain Cap Line on the External Surface of the Body of PRV 120

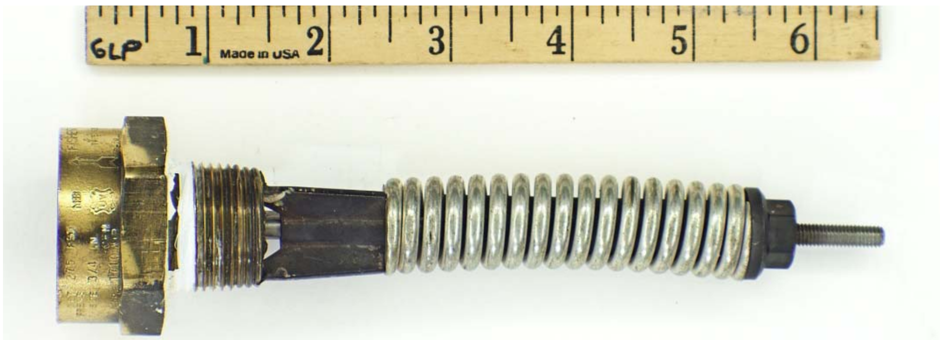

Figure 29 - External Surface of Valve Body that had been Buffed after Removal from Service; Unable to Determine if Rain Cap had been Present in PRV 5

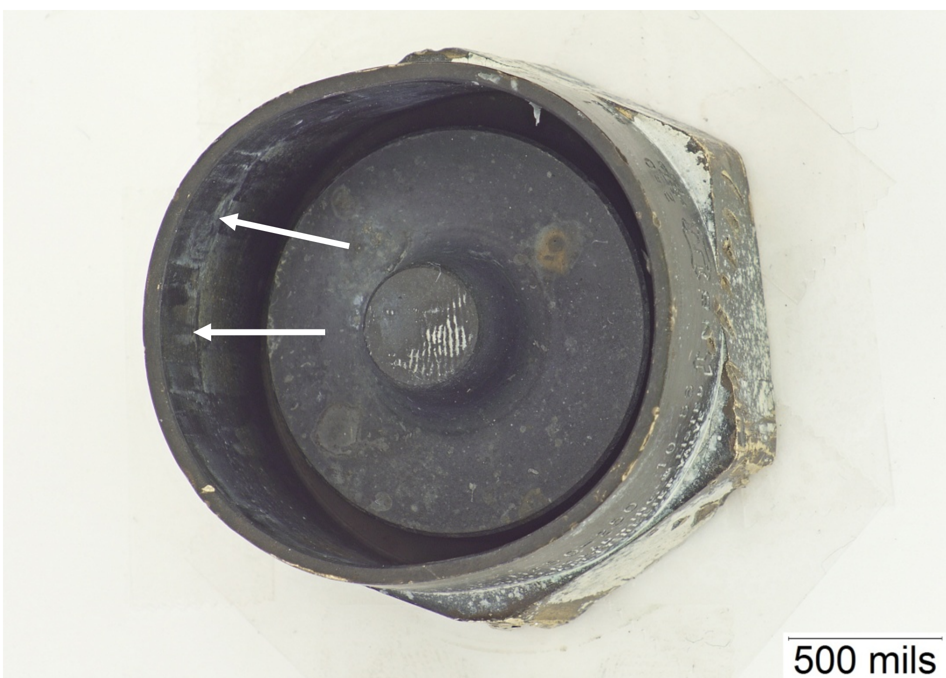

Figure 30 - Faint Rain Cap/Plug Line on the Internal Surface of the Body of PRV 350

Figure 31 - Internal Rain Cap/Plug on PRV 350

4.4 Summary of Findings

Table 15 presents a summary of the detailed examinations of the PRVs that that demonstrated performance issues (did not open by 375 psig; exhibited high start-to-discharge pressure or low-start-to-discharge pressure per UL 132 criteria for new valves) during the initial pressure testing program and a summary of the results are provided in the following subsections.

4.4.1 PRVs that Did Not Open

The analysis of the PRVs that did not open by the test pressure of 375 psig in the initial performance testing program revealed a number of conditions that may have contributed to this behavior. These conditions include

- Corrosion,
- Interaction between the valve stem and the guide spacers (perhaps resulting from misalignment), and
- Sticking of the gasket to the valve body.

However, for only one of the PRVs (PRV 62) was there conclusive evidence for the demonstrated behavior. In PRV 62, which is an external type PRV, the spring and sleeve were severely corroded and the corrosion products essentially 'locked' the spring and sleeve within the valve body. As discussed previously, PRV 350 had a high spring load and a greater installed displacement indicating the PRV factory set pressure was set high. PRV 350 also showed signs of mild corrosion, a stuck gasket, and possible misalignment.

For the other PRVs examined, a combination of two or more of the conditions mentioned previously may have contributed to the 'sticking' closed behavior of the valve; however none of the evidence was conclusive. The results of the examinations of the PRVs that did not open during initial pressure testing are presented in Appendix A.1.

4.4.2 PRVs that Exhibited High Start-to-Discharge Pressure Behavior

Twelve PRVs that exhibited high start-to-discharge pressures were examined to determine conditions that would conclusively explain the behavior. Most of these PRVs initially discharged at a high start-to-discharge pressure but opened in subsequent trials near or below the set pressure. The examinations revealed several conditions that may have contributed to the high start-to-discharge pressure. Those conditions include

- Corrosion,
- Interaction between the valve stem and the guide spacers,
- Possible valve stem misalignment, and
- Sticking of the gasket to the valve body.

However, the evidence was conclusive for only one of these PRVs (PRV 398). PRV 398 had a zinc coated spring and valve stem with significant amounts of zinc corrosion products on the valve stem and guide spacer that likely resulted in the high start-to-discharge pressure behavior. PRV 41 exhibited a strong interaction zone between the valve stem and the guide spacer that could have caused the valve to exhibit high start- to-discharge behavior. The results of the examinations of the high start-to-discharge PRVs are presented in Appendix A.2.

The high start-to-discharge behavior followed by more normal opening and sealing behavior is not unexpected for devices that have different materials in contact under static loads for extended periods of time even if extensive corrosion or material transfer has not occurred. There may be treatments such as the use of dry film lubricants or corrosion prevention compounds (CPCs) that might mitigate some of these issues; however, treatments and exposure experiments would need to be conducted to assess the possible benefits.

4.4.3 PRVs that Exhibited Low Start-to-Discharge Pressure Behavior

Eleven PRVs that exhibited low start-to-discharge pressures were examined and for only one of the eleven PRVs examined was there conclusive evidence for the demonstrated behavior. That valve was PRV 211 which had a broken gasket and leaked immediately when pressurized. This situation was described in Section 4.2 and illustrated in Figures 10 through 12. However, the cause of the broken gasket under service conditions could not be determined from the evidence obtained in this study. Because no conclusive evidence for the low start-to-discharge behaviors of the other PRVs examined was uncovered detailed descriptions of the results of the examination are not included in Appendix A.

Table 15 – Summary of Detailed Examinations of PRVs

PRV ID	PRV AGE (yrs)	REASONS FOR DEMONSTRATED BEHAVIOR
PRV Did Not Open by 375 psig		
279	**17**	No conclusive evidence.
350	**22**	Mild corrosion, stuck gasket, possible misalignment, high spring load and displacement indicating the PRV set pressure was set high.
5	**28**	No conclusive evidence.

PRV ID	PRV AGE (yrs)	REASONS FOR DEMONSTRATED BEHAVIOR
274	43	Interaction between the valve stem and guide spacer, possible misalignment – inconclusive.
292	43	Possible misalignment – inconclusive.
173	44	Mild corrosion, interaction between the valve stem and guide spacer, misalignment, stuck gasket – inconclusive.
326	45	Mild corrosion, interaction between the valve stem and guide spacer, stuck gasket – inconclusive.
250	51	Sticking gasket – inconclusive.
102	52	Mild corrosion, interaction between the valve stem and guide spacer, possible misalignment – inconclusive.
62	57	Conclusive evidence of severe corrosion that 'locked' the spring and sleeve to the valve body.
PRV Exhibited High Start-to-Discharge Pressure		
202	6	No conclusive evidence.
351	12	Lightly stuck gasket – inconclusive.
132	13	No conclusive evidence.
398	19	Extensive zinc corrosion products on valve stem and guide spacer caused sticking.
19	25	Mild corrosion, possible misalignment – inconclusive.
41	29	Somewhat extensive interaction region (oxidation) between the valve stem and spacer guide that stuck and then broke loose.
407	32	No conclusive evidence.
343	42	No conclusive evidence.
270	45	No conclusive evidence.
268	52	No conclusive evidence.
251	53	No conclusive evidence.
PRV Exhibited Low Start-to-Discharge Pressure		
262	4	No conclusive evidence.
383	5	No conclusive evidence.
443	6	No conclusive evidence.
468	8	No conclusive evidence.
211	11	Conclusive evidence of broken gasket in PRV.
349	15	No conclusive evidence.
329	36	No conclusive evidence.
396	36	No conclusive evidence.
57	47	No conclusive evidence.
56	48	No conclusive evidence.
New PRV		
146	New	No conclusive evidence.

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APPENDIX A

DETAILED VISUAL EXAMINATIONS OF PRVS

A.1 Detailed Visual Examinations of PRVs that Did Not Open in Initial Performance Test Program

This section documents the detailed visual examinations of the PRVs that did not open in the original performance testing program. The valves documented here include: PRV 62, PRV 173, PRV 274, PRV 326, PRV 350, PRV 102, PRV 279, PRV 292, PRV 250, and PRV 5.

PRV 62

PRV 62 is an external, ¾-inch PRV with a 250-psig set point. The manufacturer of this valve was reported as “other” and the propane tank size and location were not reported. The climate conditions were reported as warm and dry. The PRV had been in service for 57 years. It did not have a rain cap or evidence of a rain cap line. This PRV did not open when tested to 375 psig during the initial study and again did not open when retested to 375 psig under the new ‘real world’ test conditions (see Table 6). Furthermore, it did not open when subsequently pressurized with air to 500 psig. Instead, the PRV was mechanically opened using an Instron testing machine. The PRV eventually opened at a machine load of 550 pounds with a displacement of about 0.02 inch.

Visual examination of PRV 62 revealed that the spring was severely corroded as is shown in Figures A-1 and A-2. The external surfaces of the brass valve body were not severely discolored or corroded after the 57 years of service; however the external surface of the valve body had been buffed or abraded with a fine wire brush to read the valve data on the body. The locking mechanism was a notched ring with spanner notches that screwed into the top of the valve body. There was no evidence of either tack welds or drive pins to hold the locking ring in place, but it appeared that the locking ring had not been tampered with.

During the initial attempts to disassemble PRV 62, the locking ring could not be readily removed. Consequently, the valve body was machined away below the locking ring to release the spring. When that machining was completed, only the top three coils of the spring released. The coils further down in the valve body did not move; they were locked in place by the severe corrosion that had occurred. The spring was eventually removed by pushing it out using a plunger in the Instron machine. A load of 832 pounds was required to start moving the spring. Figure A-3 shows the scrape marks in the corrosion products on the inside surface of the valve body. Figure A-4 shows that a sleeve was on the portion of the spring that was deep in the valve body and the severe corrosion on the sleeve and the spring coils below the sleeve. The surface of the gasket and the rusted screw through the gasket from PRV 62 is shown in Figure A-5. It contains some white deposits on its surface.

The examination of PRV 62 has conclusively shown that the internal components were so severely corroded that they were locked in place.

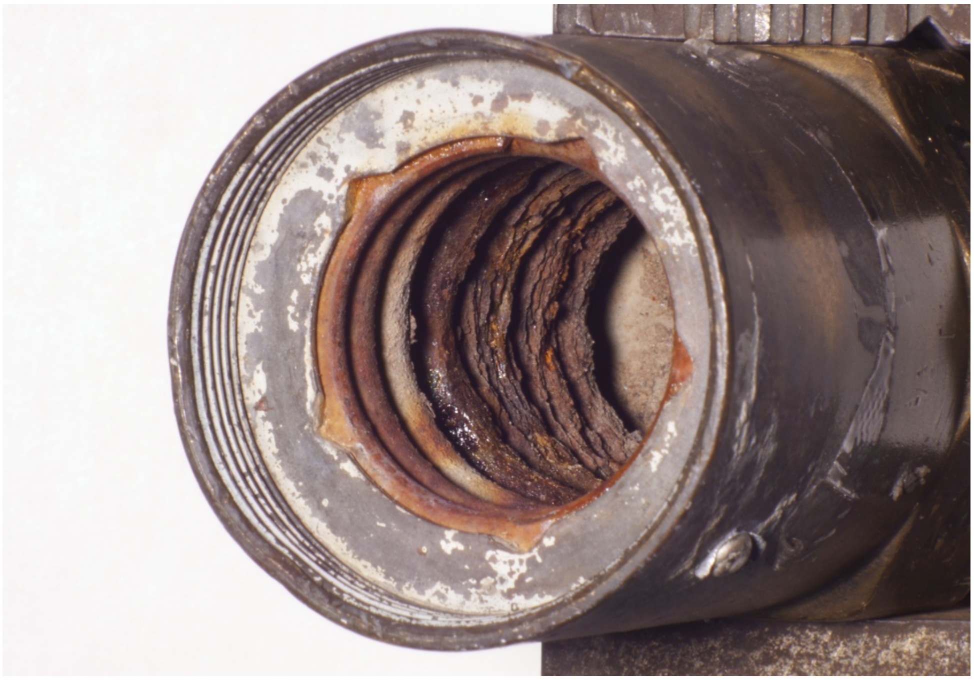


Figure A-1. Severe Corrosion of the Spring in PRV 62

Figure A-2. Higher Magnification View of the Corrosion of the Coils in Spring in PRV 62

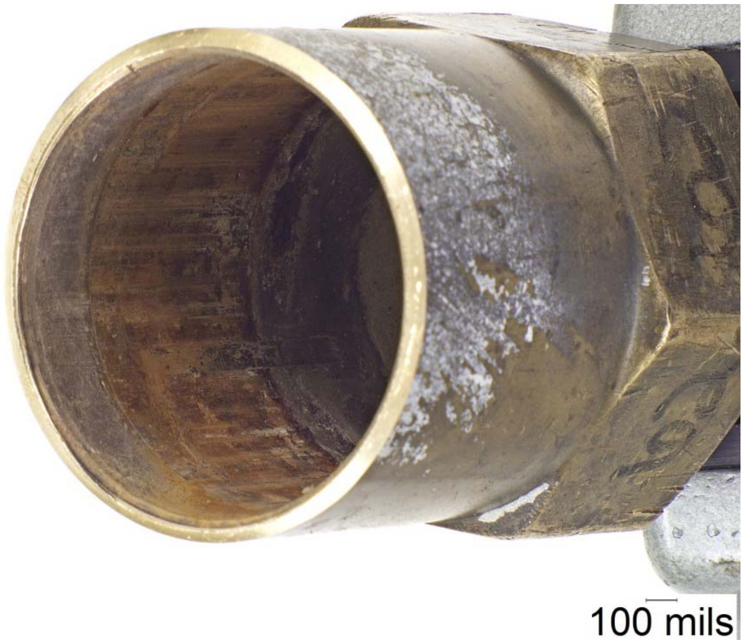


Figure A-3. Internal Surface of the Valve Body from PRV 62 after the Spring was Removed

Figure A-4. Corroded Spring and Sleeve Surrounding the Spring from PRV 62

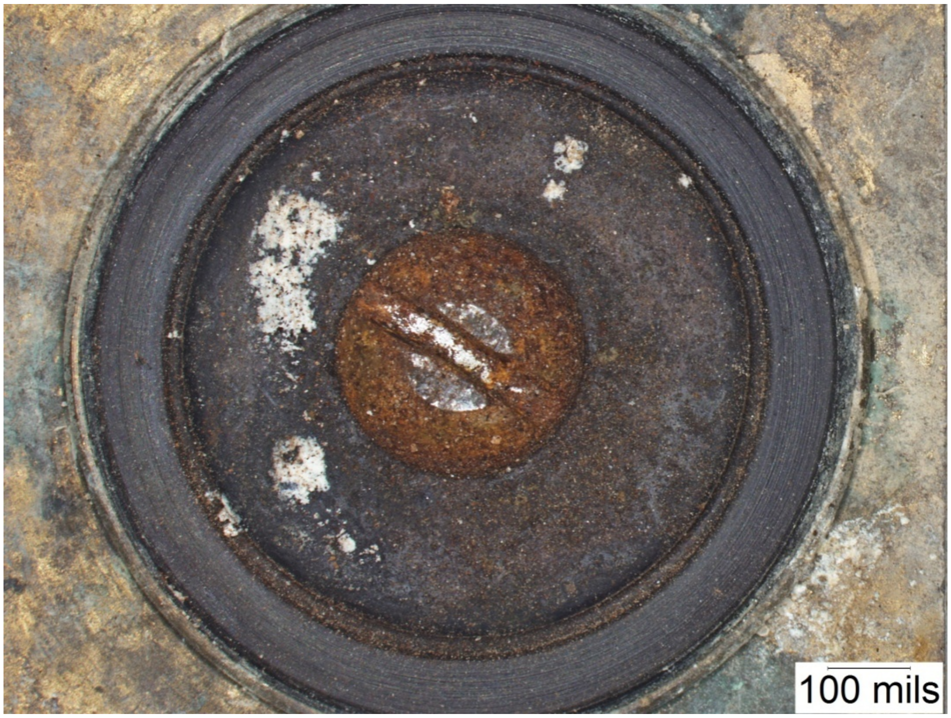


Figure A-5. Gasket Surface and Corroded Screw from PRV 62

PRV 173

PRV 173 is an internal, ¾-inch 250-psig set point PRV. It was produced by Manufacturer A and had been in service for 44 years in a 250-gallon tank located in a warm, damp climate. It did not have a rain cap when provided and there was no external or internal rain cap line. This PRV did not open at 375 psig when tested during the initial study; however, it did open when retested during the present study at 347 psig using a slow pressure rise and applied heat (see Table 6). Initial visual examination revealed slight discoloration of the internal surface of the valve body and some debris in the valve body. The internal surface of the valve body had silver and white paint on it and the weep hole was plugged with white paint. The portion of the valve stem that was visible was not corroded. The spring was coated with green coating and was not corroded. The locking mechanism was a single drive pin through the adjusting nut and the valve stem. There was no evidence of tampering with the locking mechanism.

When PRV 173 was disassembled, the valve stem and seat disc holder were stuck in the valve body. The valve stem could be wiggled slightly but it did not release from the valve body. Subsequently, the stem was pushed out of the valve body in an Instron machine; a load of 20 pounds was required to break it loose. This was somewhat surprising because this valve had opened when it was retested during the present study. Figure A-6 shows the valve stem and the spacer prior to pushing it out of the valve body. There was one region of corrosion on the valve stem below the spacer and under the spring. Figures A-7 and A-8 show another region of corrosion/interaction between the guide washer at the lower end of the spacer and the valve stem. That corrosion/interaction may have caused or contributed to the did-not-open behavior when initially tested or the high-start-to-discharge pressure when the PRV was retested during the present study. However, the failure investigator believes that the interaction line may be indicative of a valve stem alignment problem with the spacer and guide washers used with this manufacturer's design.

Figure A-6. PRV 173 after the Spring had been Removed Showing Discoloration of the Spacer and Corrosion on the Valve Stem (Arrow)

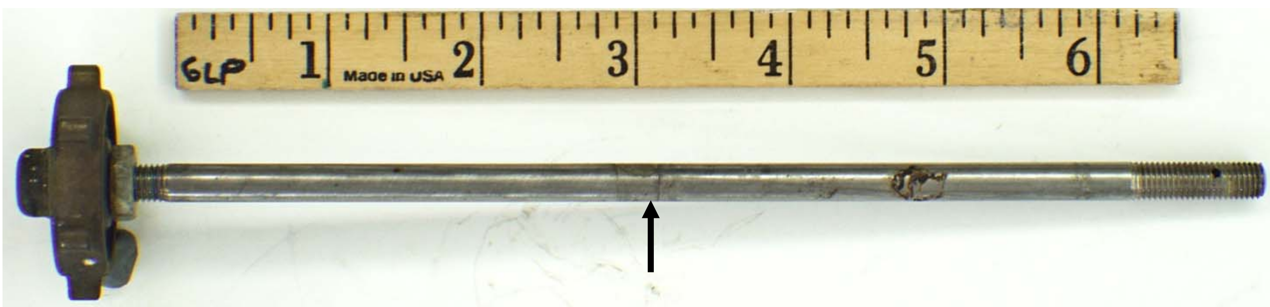


Figure A-7. PRV 173 Valve Stem after Spacer was Removed Showing an Interaction Line and Corrosion Between the Spacer Washer and the Valve Stem

Figure A-8. Higher Magnification view of the Corrosion Interaction Line Between the Valve Stem and the Guide Washer at the Lower End of the Spacer

Another factor that may have contributed to the performance of PRV 173 was the gasket (seat disc). The gasket was stuck in the disc holder and broke into many small pieces when pried up and pulled on to remove it. The portion of the gasket remaining in the holder after many small pieces tore off is shown in Figure A-9. Thus, the gasket may also have been stuck to the seat sealing surface causing the PRV to be 'stuck' shut in the original test program and to open at a high start-to-discharge pressure when retested under the 'real world' test conditions.

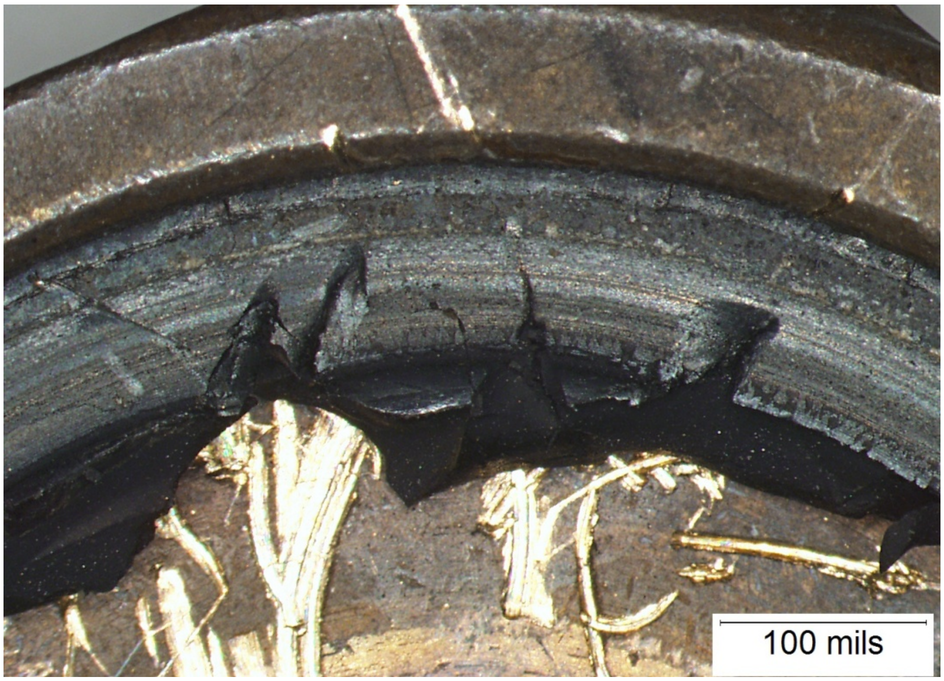


Figure A-9. Portion of the Gasket Stuck in the Seat Holder from PRV 173. ***This gasket contained radial cracks in the outer circumferential ring and it broke into many small pieces when it was puled to remove it from the holder***

PRV 274

PRV 274 is a ¾ inch, 250-psig-set-point internal valve. It was produced by Manufacturer A and had been in service for 43 years in a 325-gallon tank located in a suburban environment described as cold and damp. It did not open at 375 psig when tested during 2009; however, it did open at 328 psig when tested during the present study with a slow pressure rise and applied heat (see Table 4).

PRV 274 prior to disassembly is shown in Figure A-10. The inner and outer surfaces had been painted silver. A rain cap was not present and there was no indication of an internal or external rain cap line. Some of the green coating on the spring had flaked off and some rust was present on the spring surface. The spacer between the body and the top of the spring was somewhat discolored and contained a small amount of rust. The spacer was made from sheet metal that had been rolled to form the slotted cylinder. The set-point-locking mechanism was a single drive pin through the nut and the stem. There was some corrosion on the drive pin. There was no evidence of tampering of the locking mechanism.

When PRV 274 was disassembled the valve stem and poppet did not release from the valve body. The stem could be wiggled slightly but it was stuck in the valve body. Subsequently it was pushed out in the Instron machine and a load of 56.9 pounds was required to free it. This behavior was similar to that of PRV 173, but the load required was much higher.

Examination of the valve stem after disassembly revealed that there was a corroded/discolored region in the surface that had been covered by the spring and a corrosion/interaction region between the valve stem and the guide washer at the lower end of the spaces. Those regions are illustrated in Figures A-11 through A-14. Another factor that may have contributed to the behavior of PRV 274 was that there was evidence that some of the gasket material was transferred on to the valve-body seat surface, as shown in Figure A-15.

The investigator believes that the interaction region between the guide washer and the valve stem is indicative of possible mis-alignment issues with this PRV design.

Figure A-10. PRV 274 Did Not Open when Tested during the Initial Study but Opened at 328 psig when Retested During the Present Study

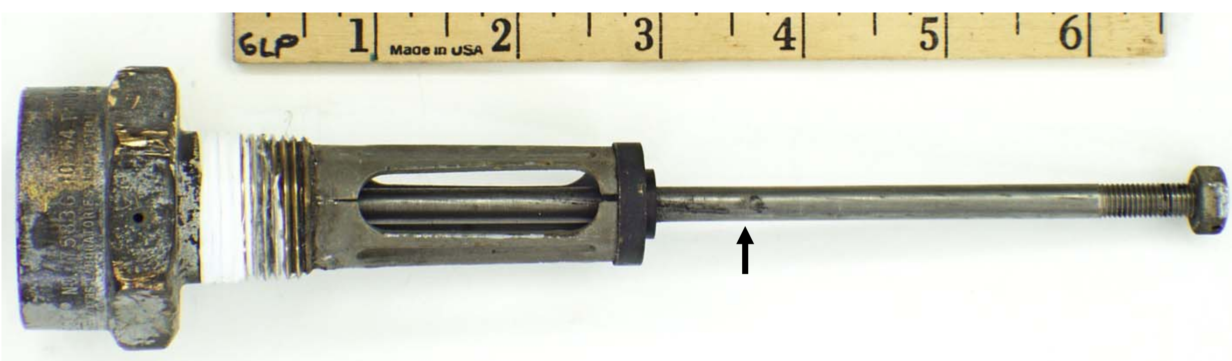


Figure A-11. PRV 274 after the Spring was Removed Showing Corrosion on the Valve Stem Below the Spacer (Arrow)

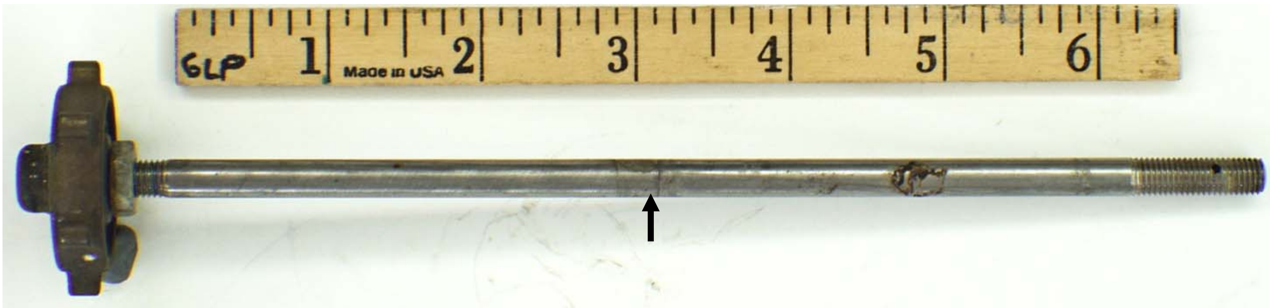


Figure A-12. Valve Stem from PRV 274 Showing Corrosion/Interaction Region between the Guide Washer and the Valve Stem (Arrow)

Figure A-13. Higher Magnification View of the Corrosion/Interaction Region between the Valve Stem and the Guide Washer from PRV 274

Figure A-14. Region of Interaction between the Valve Stem and the Guide Washer 180 Degrees from the Region Shown in Figure A-13, PRV 274

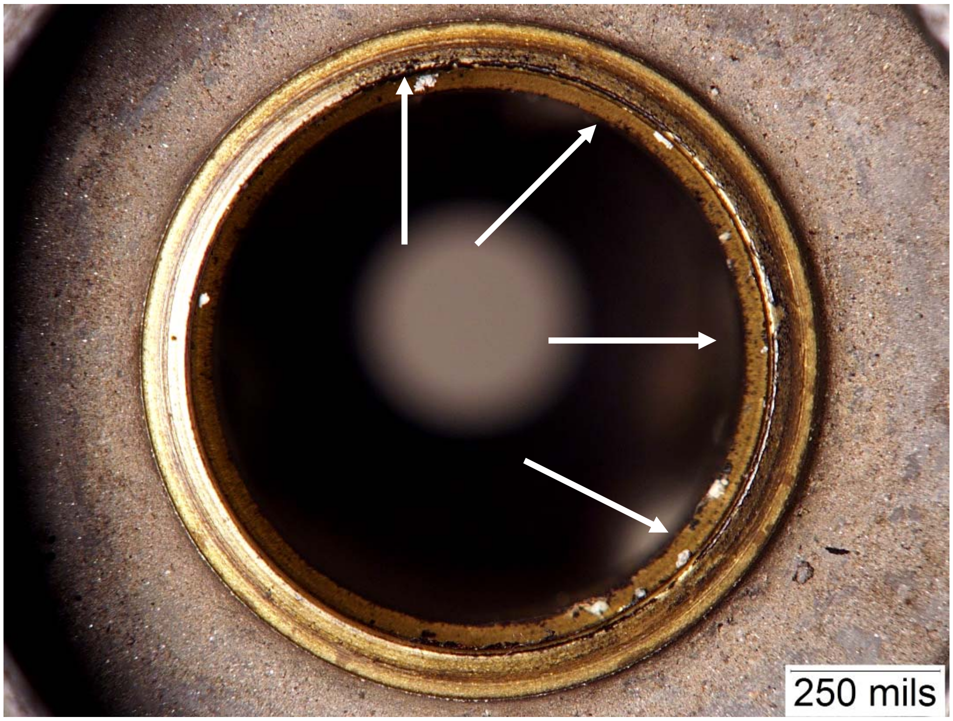


Figure A-15. Valve Body Seal Seat Surface from PRV 274 Showing Gasket Material Transfer

PRV 326

PRV 326 is a ¾-inch, 250-psig internal valve that was produced by Manufacturer A. It had been in service for 45 years in a 250-gallon tank in a rural environment described as warm and damp. A rain cap was not provided with this PRV and there was no rain cap line evident. This PRV did not open when tested to 375 psig during the initial study, but it did open at 355 psig when tested with a slow pressure rise and heat during the present study (see Table 4).

After retesting, PRV 326 was visually inspected and then disassembled. Figure A-16 shows the appearance of PRV 326. The internal and external surfaces of the valve body had been painted silver and there was an O-ring (painted silver) at the top of threaded region of the valve body. The weep hole was plugged and the poppet was somewhat discolored but there was no loose corrosion or debris in the valve body. The light green coating had rubbed or flaked off some areas of the spring and corrosion of the spring had occurred in those regions. There was some corrosion on the surfaces of the spacer located between the valve body and the spring.

There also was corrosion on the top guide washer and on the valve stem at the lower end of the spacer as shown in Figure A-17. Rust was also present on the bottom surface of the bottom guide washer adjacent to the adjustment nut. The locking mechanism was a drive pin through the nut and the valve stem; the drive pin was corroded. There was no evidence of tampering with the adjustment nut. Figure A-18 illustrates the various corroded regions on the valve stem and Figure A-19 shows the corrosion/interaction region between the valve stem and the guide washer at the lower end of the spacer. That region is similar to the regions shown on the valve stems of PRV 173 and PRV 274. In addition, Figure A-19 also shows another region of corrosion on the valve stem below the corrosion/interaction region. This corrosion most likely contributed to the behavior of this PRV during testing. In addition, the gasket from the PRV was brittle and broke into many pieces when pulled from the valve with pieces remaining stuck in the disc holder. It appeared similar to the gasket in PRV 173 shown previously in Figure A-9.

Figure A-16. Appearance of PRV 326

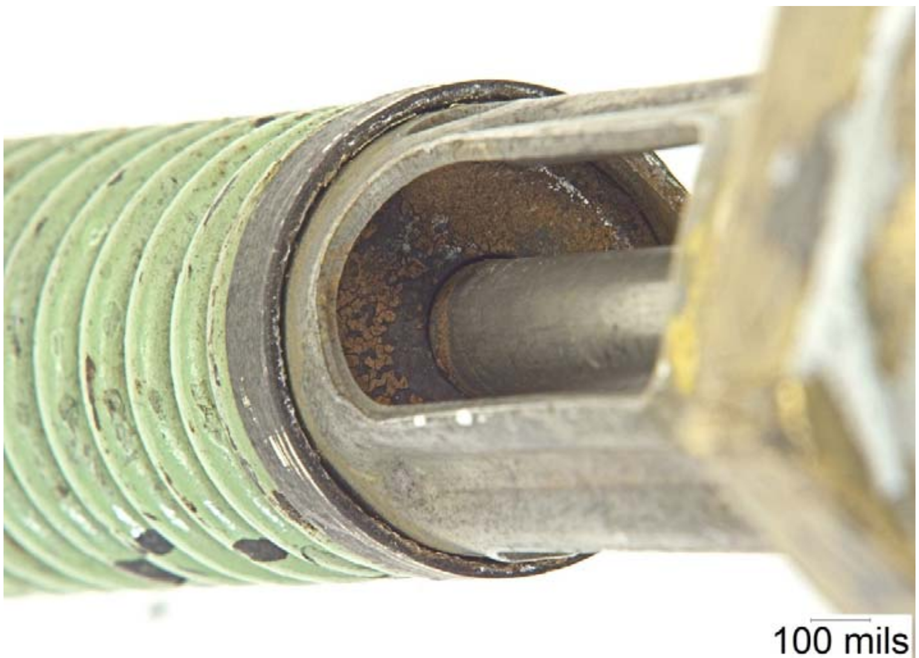


Figure A-17. Corrosion on the Top Surface of the Guide Washer and the Valve Stem at the Lower End of the Spacer in PRV 326

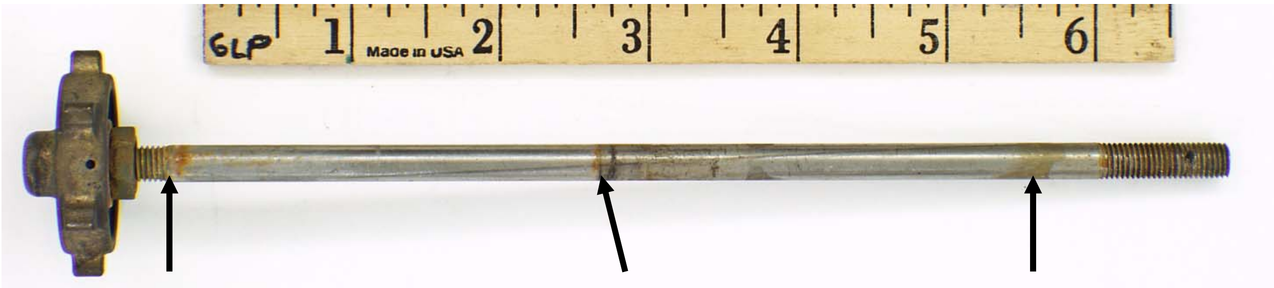


Figure A-18. Corrosion/Interaction Region on the Valve Stem from PRV 326

Figure A-19. Corrosion/Interaction Line on the Valve Stem at the Location of the Guide Washer (Arrow) and Additional Corrosion on the Valve Stem Below That Region

PRV 350

PRV 350 is a one-inch, 250-psig set point internal valve that had been produced by Manufacturer B. The valve had been in service for 22 years in a 500-gallon tank in a rural environment that was listed as cool and damp. A rain cap/plug, which fits inside the valve body and overlapped the outside of the PRV, was provided. PRV 350 did not open when tested during the initial study but it did open at an initial start-to-discharge pressure of 352 psig when conditioned with propane during the present study (see Table 5).

The appearance of PRV 350 is shown in Figure A-20. Visual examination of PRV 350 revealed that the external and internal surfaces of the brass valve body, brass spacer, and brass gasket holder were discolored; they were almost black. There was no debris inside the valve body but there were some white surface deposits on the gasket holder. The valve body was distorted to an oval shape as is shown in Figure A-21. The spring had a purple coating and much of the coating had flaked off and there was no sleeve in the spring (the investigator believes that sleeves were present inside the springs and around the valve stem to minimize buckling of the spring when the valve opening pressure was set). The locking mechanism was a drive pin through the adjustment nut and valve stem. The adjustment nut and the threads on the valve spring beyond the nut were slightly corroded, but there was no evidence of tampering with the adjustment nut.

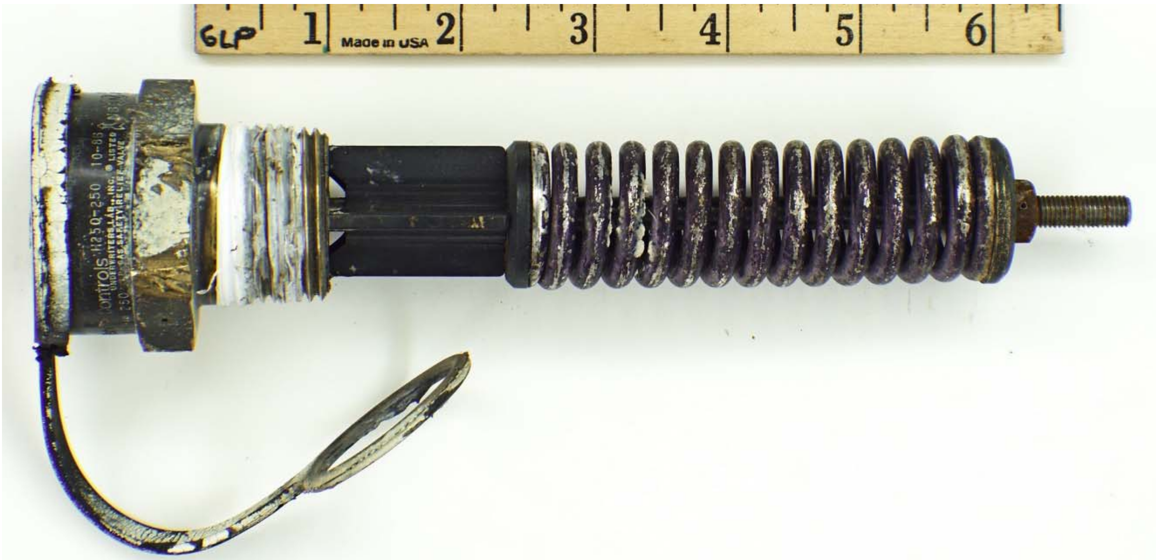


Figure A-20. Appearance of PRV 350 Including Its Rain Cap

Figure A-21. Distorted Valve Body from PRV 350. ***Note the significant discoloration of the internal surfaces of the valve body and also the seat disc holder.***

When PRV 350 was disassembled, the valve stem and valve set were loose. Figure A-22 shows corroded regions on the valve-stem surface at two magnifications. The higher magnification view (Figure A-23) shows the region where the valve stem contacted the inner surface of brass guide spacer. Figure A-24 shows the gasket removed from the valve. It shows that the compression set rings were somewhat off center, perhaps indicating valve stem alignment problems. Figure A-25 shows a region of pullout of the gasket material from the surface of the gasket and Figure A-26 shows staining and gasket material transfer to and from the gasket to the valve body surface of PRV 350. Thus, this analysis suggests three factors that likely contributed to the did not open and high-start-to-discharge conditions of PRV 350 during the pressure testing conducted during the initial study and the present study, respectively. Those conditions were: (1) corrosion of the valve stem and the guide spacer; (2) sticking of the gasket to the valve body sealing surface, and (3) possible misalignment of the valve that caused binding between it and the spacer guide.

Figure A-22. Corrosion on the Surface of the Valve Stem from PRV 350

Figure A-23. Higher Magnification View of Some of the Corrosion on the Valve Stem from PRV 350

Figure A-24. Sealing Surface of the Gasket from PRV 350 Showing That the Compression Set Lines Were Somewhat Off Center Indicating Possible Alignment Problems

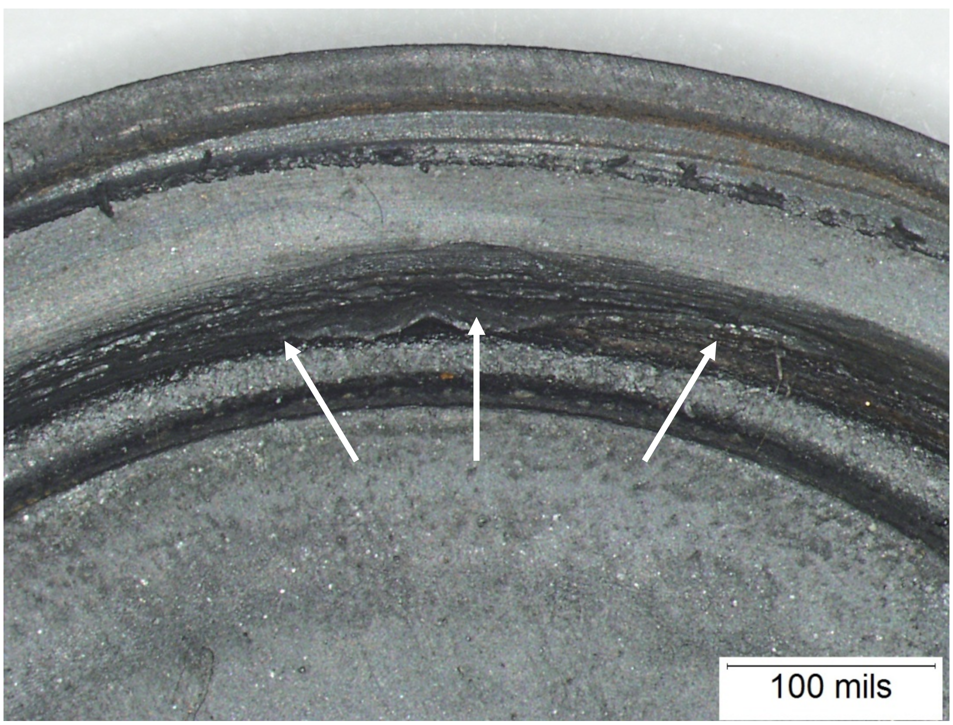


Figure A-25. Pullout Regions (Arrows) from the Surface of the Gasket from PRV 350

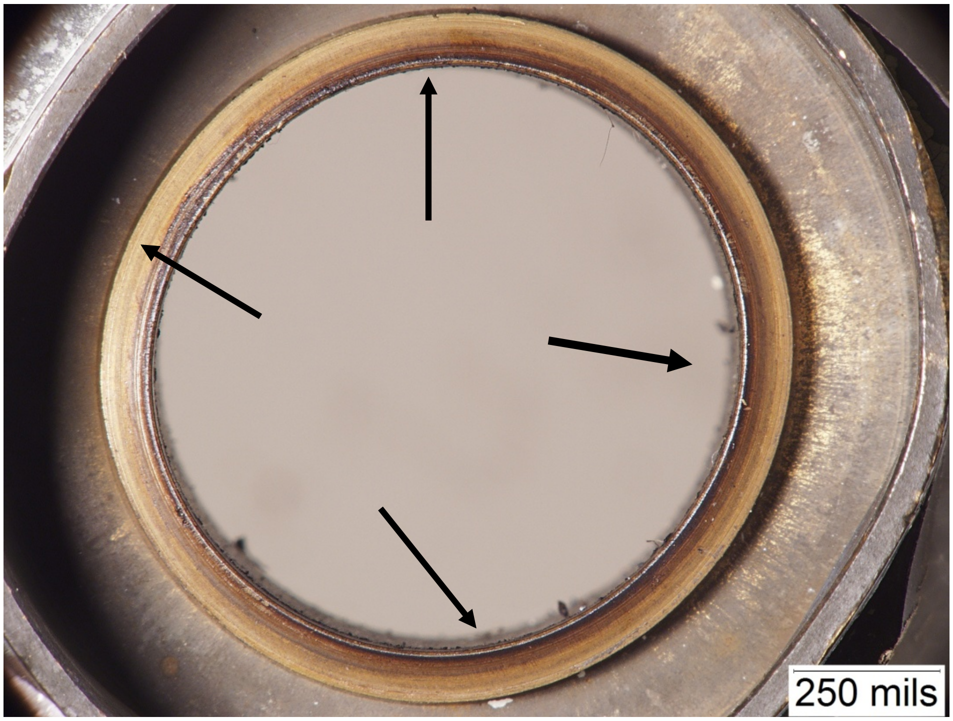


Figure A-26. Stains from the Gasket and Region of Gasket Material Transfer onto the Valve Body Sealing Surface of PRV 350

PRV 102

PRV 102 is a one-inch, 250-psig set point internal valve produced by Manufacturer A. PRV 102 had been in service for 52 years in a 500-gallon tank in a rural environment described as cool and damp. The tank was an above-ground tank and was located in the full sun. The rain cap was not included with this PRV. PRV 102 did not open at 375 psig when it was tested during the initial study, but it did open at a pressure of 308 psig when retested with the slow pressure rise and applied heat procedures during the present study (see Table 6).

Visual examination of PRV 102 revealed dried mud on the internal surfaces of the valve body and mud and debris in the valve body below the valve sealing region. The presence of the mud indicates that the valve may have been dropped into mud after it was removed from the tank. Those features are shown in Figures A-27 and A-28, respectively. There also was blue paint on the outside surface of the valve body. The spacer guide in this PRV was a three-finned brass component. The other valves examined during this study produced by Manufacturer A had tubular spacers. The spring was gold color and there was some white residue on the spring surface and debris inside the spring, as shown in Figures A-29 and A-30. There was a sleeve inside the spring and the locking mechanism was a drive pin through the adjustment nut and the valve stem. There was no evidence of tampering with the adjustment nut.

Figure A-27. Appearance of PRV 102. ***Note the absence of corrosion or discoloration of the components.***

Figure A-28. White Residue on the Spring Coil Surfaces and Debris Inside the Spring

Figure A-29. Blue Paint on the External Surface and Dried Mud on the Internal Surface of PRV 102. ***A faint internal rain cap line was present(arrows)***

Figure A-30. Debris in the Valve Body Below the Sealng Surface

When PRV 102 was disassembled, the valve stem and poppet popped free from the valve body. There was considerable corrosion on the surface of the valve stem and a distinct interaction mark where the surface of the valve stem contacted the inner surface of the brass guide spacer. Those features are illustrated in Figures A-31 through A-34.

Figure A-31. Corrosion on the Surface of the Valve Stem from PRV 102

Figure A-32. Higher Magnification View of the Corrosion and Interaction Region on the Valve Stem from PRV 102. ***The interaction region is where the valve stem contacts the inner surface of the guide spacer.***

Figure A-33. Corrosion/Interaction Marks on the Surface of the Valve Stem from PRV 102. ***This region was 180 degrees from the area shown in Figure A-30.***

Figure A-34. Higher Magnification View of Another Region of corrosion on the surface of the Valve Stem from PRV 102

Based on the results of these examinations, it appears that corrosion and possible misalignment contributed to the behavior of PRV 102 during pressure testing.

PRV 279

PRV 279 was a ¾-inch, 250-psig set point internal valve that was produced by Manufacturer A. It had been in service for 17 years in a 500-gallon, above-ground tank that was located in a rural environment that was described as cool and damp. The valve had an internal rain cap. PRV 279 did not open at 375 psig during the initial study and it was disassembled after that study. During the present study, the components of PRV 279 were reexamined in an attempt to identify the cause(s) for it not opening at 375 psig. This valve had an internal rain cap.

Visual examination of PRV 279 revealed that the surfaces of the valve body and the seat gasket holder were discolored during service. Debris was present in the valve body. The surface of the spring had a shiny black coating with no evidence of corrosion. The spacer was fabricated into a slotted tube from sheet metal and it contained white corrosion products, most likely zinc oxide, on its surface. Similar corrosion products were present on the surface of the guide washer between the spacer and the spring. There were a couple of spots of white corrosion products on the valve stem but the valve stem surface had been damaged during disassembly. The locking mechanism was a tack weld between the adjusting nut and the valve stem. There was no evidence of tampering with the adjusting nut. These factors were illustrated in the report from the previous study [19].

It was reported that when PRV 279 was disassembled, the seat disc (gasket) was stuck to the valve body. The application of torque to the valve stem loosened the gasket. The valve stem contained no regions of corrosion and there was only a faint interaction line where the stem contacted the spacer, as is shown in Figure A-35. The compression set rings in the gasket from

PRV 279 were slightly off-center as is shown in Figure A-36 and there was a region at the outer circumference of the gasket where the gasket material was missing. In addition, radial cracks were present in the outer circumferential ring of the gasket beyond the sealing surface, as is shown in Figure A-37. However, there was no evidence of gasket material transferred on to the sealing surface in the valve body.

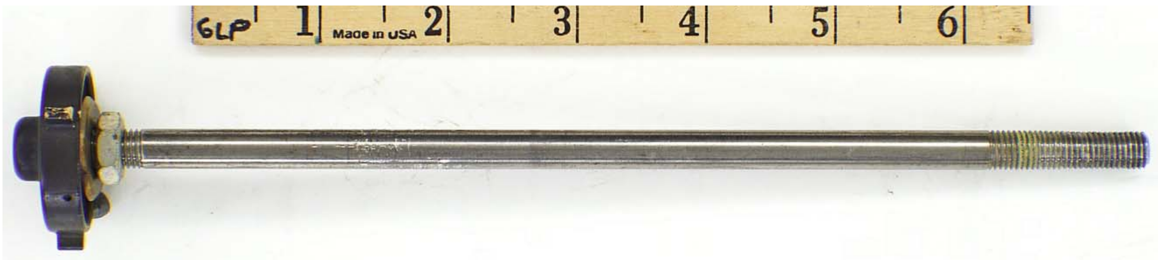


Figure A-35. Appearance of the Valve Stem from PRV 279 Showing the Absence of Corrosion and a Faint Interaction Line from Contact with the Guide Washer (Arrow)

Figure A-36. Gasket from PRV 279 Showing that the Circumferential Set Rings were Somewhat Off-Center

Figure A-37. Radial Cracks and Material Missing from the Outer Circumference of the Gasket from PRV 279

It was concluded during the initial examination of PRV 279 that there was no conclusive evidence for the sticking of the valve during pressure testing and the present study also did not reveal conclusive evidence for the sticking.

PRV 292

PRV 292 is a one-inch, 250-psig set point internal valve produced by Manufacturer G. It had been in service for 43 years in a 500-gallon, above-ground tank that was located in a rural environment described as cool and damp. A rain cap was not included with this valve. PRV 292 did not open at 375 psig during the initial study. It was visually inspected during that study but not fully disassembled. The valve stem broke at the drive pin hole through the valve stem for the locking mechanism. For safety concerns, it was not disassembled further.

During the present study, PRV 292 was visually examined and then disassembled. The appearance of PRV 292 is shown in Figure A-38. Visual examination revealed an external rain cap line and there was some dirt and debris in the valve body. The spring had a green coating and most of the coating was flaked off. Figure A-38 shows the portion of the valve stem that broke off during the initial study. This PRV had an unusual spacer between the valve body and the guide washer at the top of the spring. It was fabricated from three pieces of sheet metal that were not joined together. When the valve was disassembled those pieces fell out. There also was a screw through the top of the seat disc and that screw had been corroded, as shown in Figure A-39. The valve stem had a distinct interaction line similar to those shown previously where it contacted the upper guide washer. There was no evidence of transfer of the gasket material to the sealing surface of the valve body.

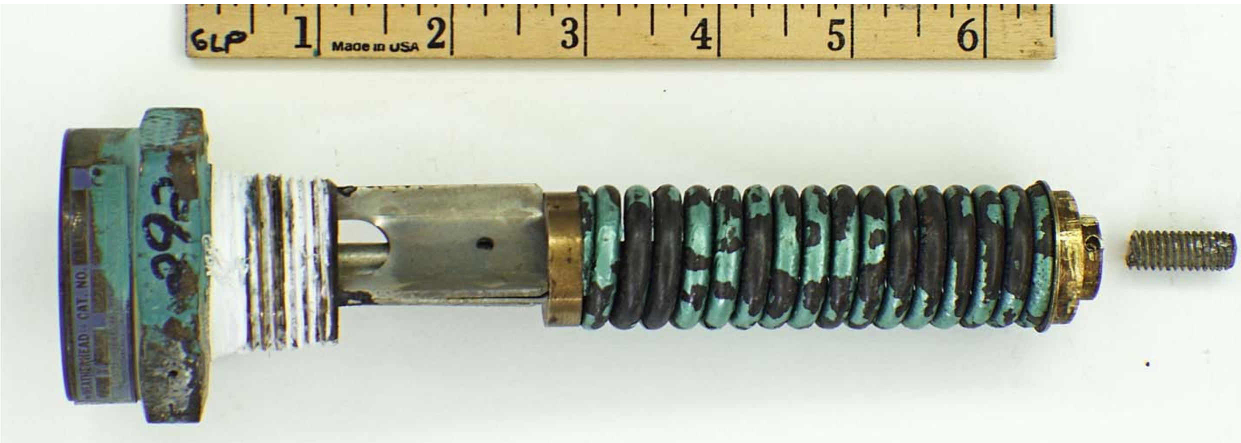


Figure A-38. Appearance of PRV 292

Figure A-39. Rusted Screw through the Gasket Holder and a Small Amount of Debris in the Valve Body of PRV 292

This examination has not shown conclusive evidence why PRV 292 stuck when pressure tested to 375 psig. The interaction line on the valve stem may indicate alignment issues but it does not appear to be sufficient enough to cause sticking at pressures 1.5 times the set pressure.

PRV 250

PRV 250 is a 250-psig set point, one-inch internal valve produced by Manufacturer A. It had been in service for 51 years in a 500-gallon above-ground tank that was located in a rural environment described as cool and damp. A rain cap was not included with the PRV. During initial performance testing program PRV 250 did not open by 375 psig. It was subjected to only one pressure cycle.

PRV 250 is shown in Figure A-40. As is shown in the figure, the external surface of the top portion of the valve body appears to have been buffed to remove the discoloration. There were small regions of discoloration on the brass spacer guide but the spring was not corroded. It was gold-colored, bright, and shiny. There was a sleeve inside the spring. The adjustment nut locking mechanism was a drive pin through the nut and the valve stem. As is shown in Figure A-41, there was corrosion and cobwebs inside the valve body. It appeared there was a faint internal rain cap line.

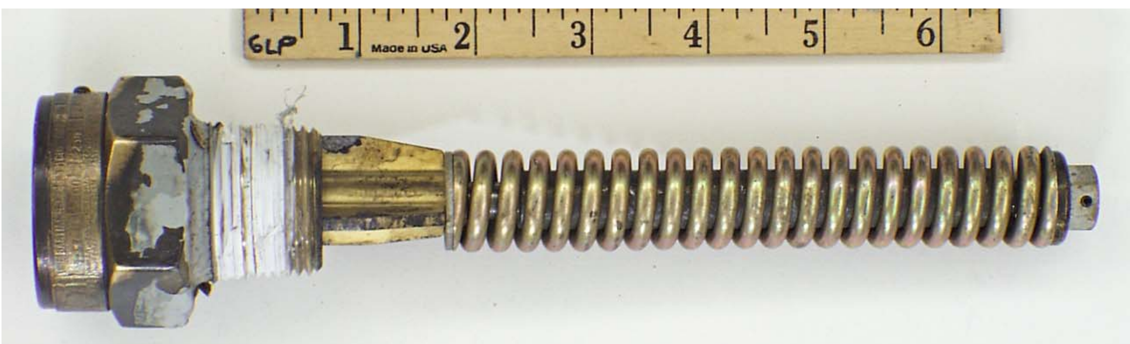


Figure A-40. PRV 250, Did Not Open During Initial Performance Testing Program

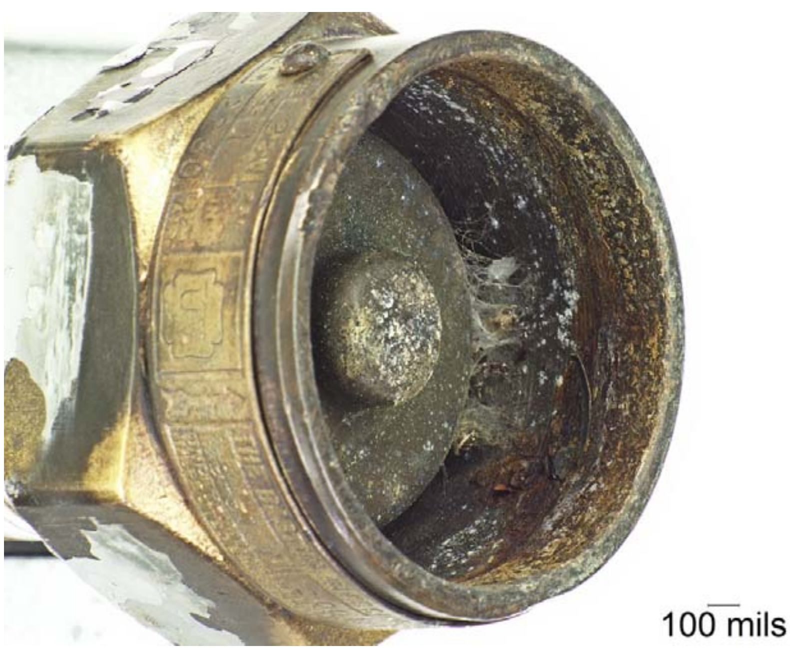


Figure A-41. Corrosion and Cobwebs in the Valve Body of PRV 250

When PRV 250 was disassembled, the valve stem/poppet was stuck to the valve body and it could not be easily loosened. Subsequently, the valve stem was pushed away from the valve body in an Instron machine and the load required to break it loose was 115.6 pounds. Based upon the area of the gasket that was exposed to the gas pressure during testing, the equivalent pressure to counteract this force was calculated to be 197-psi.

Examination of the valve body after the gasket was released showed that there was gasket material transferred to the entire inner circumference of the sealing surface as is shown in Figure A-42. As is shown in Figure A-43, there was evidence of pull out of material from the sealing region of the gasket.

There was no other conclusive evidence uncovered to explain why PRV 250 did not open when tested to 375 psig.

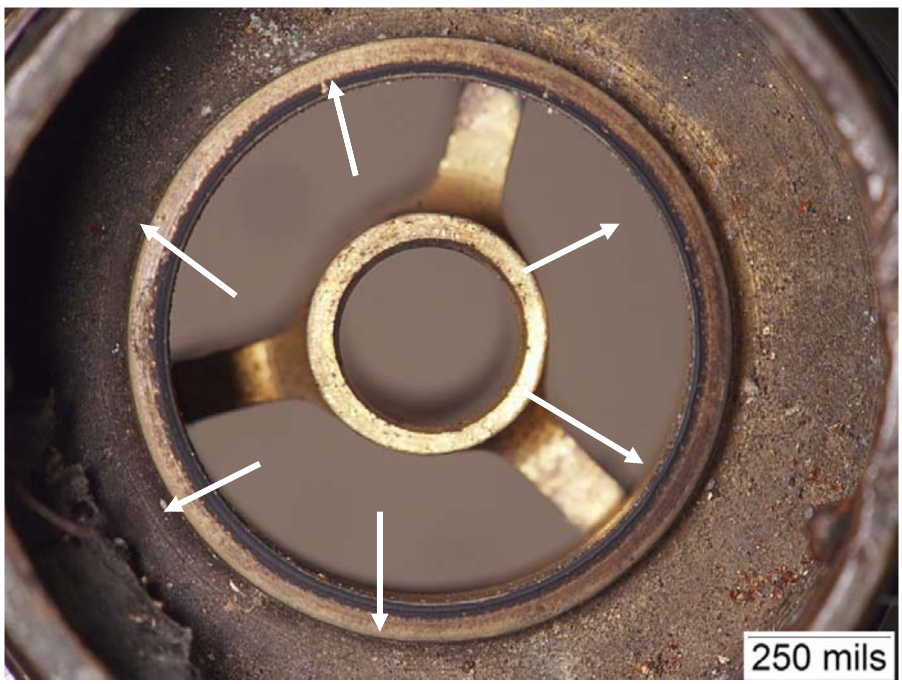


Figure A-42. Gasket Material on the Entire Inner Circumference of the Sealing Surface of the Valve Body from PRV 250

Figure A-43. Material Pulled Out of the Surface of the Sealing Region (Arrows) and Cracks in the Outer Circumferential Ring of the Gasket from PRV 250

PRV 5

PRV 5 is a ¾-inch, 275-psig set point internal valve produced by Manufacturer B. It had been in service for 28 years in a 250-gallon tank in an environment described as warm and dry. No rain cap was provided with this PRV. During initial performance testing program PRV 5 did not open when tested to 375 psig, 36-percent above its set pressure.

PRV 5 is shown in Figure A-44. The outer surface of the valve body had been buffed; thus there was no evidence of an external rain cap line. There was also no evidence of an internal rain cap line. There was a small amount of debris in the valve body and the internal surfaces were discolored. The spacer and the adjustment nut were discolored, but the spring was bright and shiny. There was no washer between the guide spacer and the spring which is common for Manufacturer B. The spring was bowed. The locking mechanism was a solid pin only on one side of the nut. There was no evidence of tampering with the adjustment nut.

When PRV 5 was disassembled, the valve stem/poppet was stuck to the valve body. It was broken loose by pushing on the valve stem in an Instron machine. The load required to release the gasket was only 31.6 pounds. That load represents a small equivalent pressure on the gasket compared to the maximum test pressure of 375 psig. There was no evidence of corrosion or an interaction line on the surface of the valve stem. There was no gasket material transferred to the sealing surface of the valve body.

The examination of PRV 5 did not reveal any conclusive evidence for the valve not opening when pressure tested to 375 psig.

Figure A-44. PRV 5. ***Note the Absence of a Washer between the Guide Spacer and the Spring and the Bow in the Spring.***

A-2 Detailed Visual Examinations of PRVs that Opened with a High Start-to-Discharge Pressure in Initial Performance Test Program

This section documents the detailed visual examinations of the PRVs that did not open in the original performance testing program. The valves documented here include: PRV 398, PRV 270, PRV 351, PRV 343, PRV 132, PRV 268, PRV 202, PRV 251, PRV 19, PRV 41, and PRV 407.

PRV 398

PRV 398 is a ¾ inch, 250-psig set point internal valve produced by Manufacturer C. It had been in service for 19 years in a 500-gallon, above-ground tank located in a rural environment described as warm and damp. A rain cap was not included with the PRV.

When tested during the initial study, PRV 398 opened at a pressure of 314 psig, about 26-percent above the set pressure.

During the present study, PRV 398 was visually inspected and then disassembled for more detailed analysis. PRV 398 is shown in Figure A-45. Examination revealed white, powdery corrosion products on the surface of the spring and on the surface of the valve stem but no evidence of red rust on either component. There were no corrosion products or debris in the valve body. The appearance of the external surface of the valve body indicated that a rain cap had been present. The adjustment/locking mechanism consisted of a single nut welded to the valve stem. Some rust was present on the locking nut. There was no evidence of tampering with the adjustment nut.

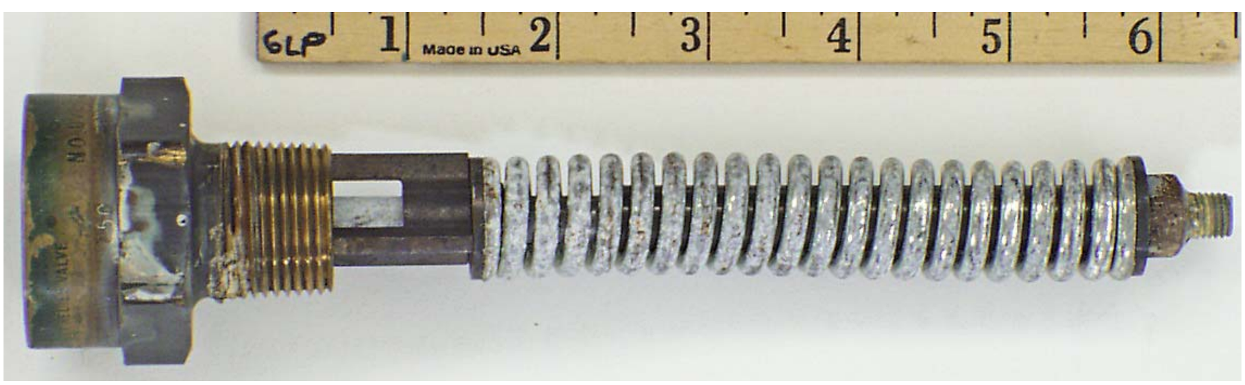


Figure A-45. Appearance of PRV 398

When PRV 398 was disassembled, the valve stem popped loose from the valve body. Figure A-46 shows the white corrosion products and rust on the surface of the valve stem and the interaction region between the valve stem and guide spacer surfaces (this region is shown at higher magnification in Figure A-47). Figure A-48 shows the white corrosion products on the inner surface of the guide spacer.

Figure A-46. White Corrosion Products, Rust, and an Interaction Band on the Surface of the Valve Stem from PRV 398

Figure A-47. Higher Magnification View of the Corrosion Products and Interaction Band on the Surface of the Valve Stem from PRV 398

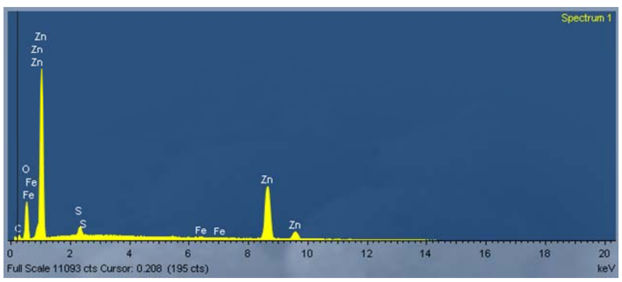
Figure A-48. White Corrosion Products on the Inner Surface of the Guide Spacer and General Oxidation of the Guide Spacer Surfaces from PRV 398

To identify the white corrosion products, some of those deposits were gently scrapped from the valve stem surface and analyzed using energy dispersive spectroscopy (EDS) in the scanning electron microscope (SEM) and by x-ray diffraction. The results of the EDS analysis are shown in Figure A-49. They show the corrosion products contained primarily zinc (Zn) and oxygen (O) with smaller amounts of sulfur (S) and iron (Fe). The carbon came from the carbon tape that was used to pull the corrosion products from the valve stem. The EDS results indicate that these corrosion products were zinc oxide.

PRV398 Corrosion 1000x

Spectrum	C	O	S	Fe	Zn	Total
Spectrum 1	6.1	20.7	2.0	0.3	70.9	100.0

All results in weight% and are normalized.
Accelerating voltage 20kV, Live time 120 seconds.



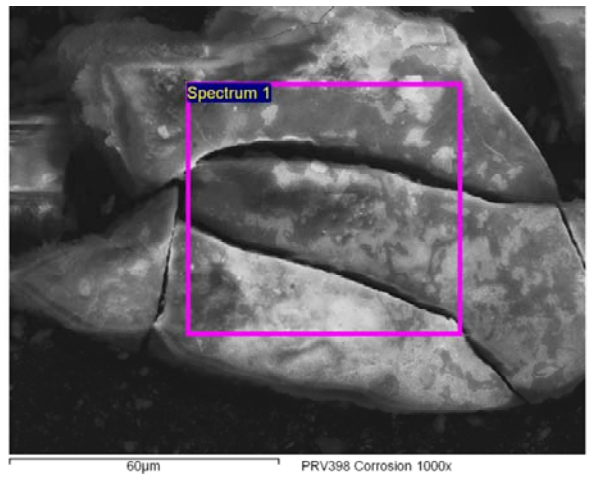


Figure A-49. Results of EDS Analysis of the White Corrosion Products from PRV 398

Another sample of the white corrosion products were analyzed by x-ray diffraction using copper k-alpha x-ray source. The results of that analysis are shown in Figure A-50. The pattern was analyzed using the Powder Diffraction File-4+ Release 2009 and the Inorganic Crystal Structure Database/NIST version 2009-2. Three zinc bearing phases were identified in this pattern. Those phases were zinc oxide (ZnO), hydrozincite, and zinc metal. The zinc metal came from the zinc coating on the valve stem. In addition, a small amount of iron sulfate was tentatively indexed in this pattern. That phase clears up several non-indexed peaks and accounted for all of the elements detected by the EDS analyses.

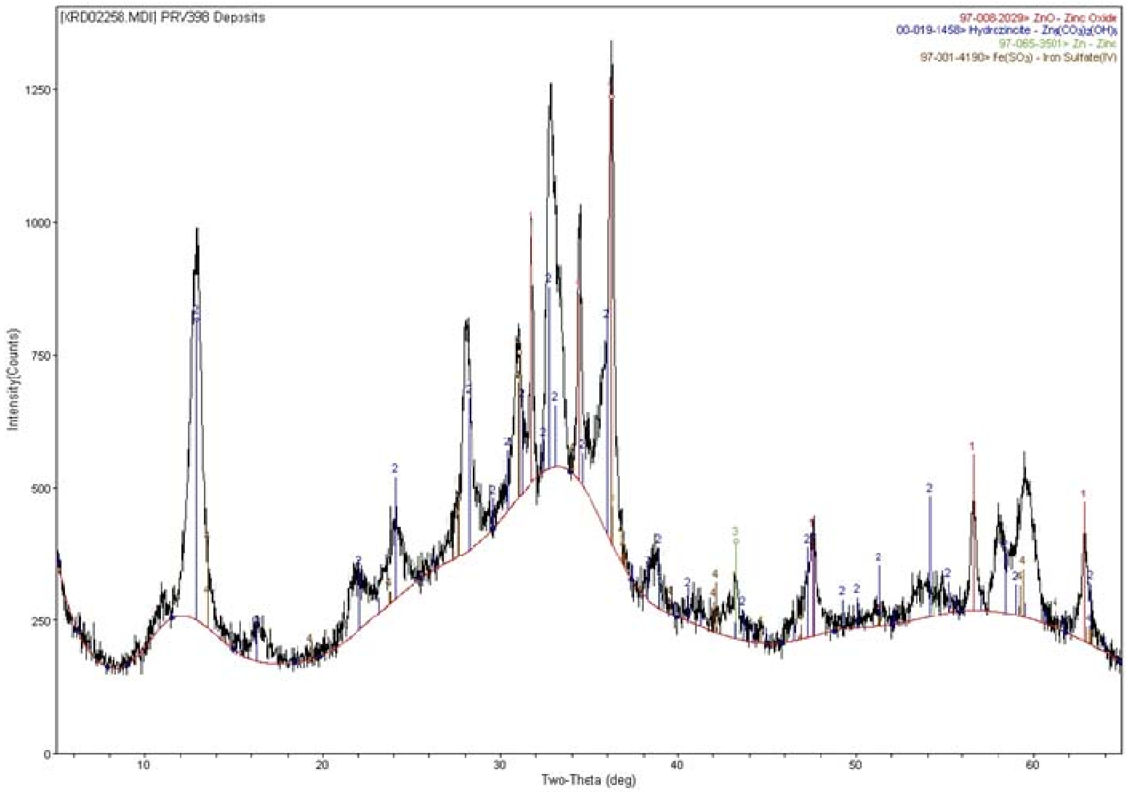


Figure A-50. X-ray Diffraction Pattern from the Corrosion Products from PRV 398

The results of the examination of PRV 398, which exhibited high-start-to-discharge pressure during pressure testing, show significant amounts of zinc corrosion products on the spring, the valve stem, and the inside surface of the guide spacer. The spring and valve stem had been coated, most likely electroplated with zinc. Those corrosion products most likely bonded the valve stem to the guide spacer which resulted in the high-start-to-discharge pressure behavior.

PRV 270

PRV 270 is a one-inch, 250 psig set point internal valve produced by Manufacturer D. It has been in service for 45 years in a 500-gallon, above-ground tank that was located in a rural environment that was described as cool and damp. A rain cap was not included with this PRV. During initial pressure testing, this valve opened at 328 psig, 31-percent higher than its set pressure. During subsequent pressure tests it opened at pressure between 185 and 199 psig, and resealed at pressures between 178 and 191 psig. Thus, after initially exhibiting high start-to-discharge behavior, PRV 270 exhibited low sealing and low start-to-discharge behavior. During the present study this valve was visually inspected and then disassembled for more detailed analysis.

PRV 270 is shown in Figure A-51. The valve body had been painted silver and there did not appear to be a rain cap line on either the external or internal surfaces. However, there was very little debris in the valve body. The spring had a green coating, some of which had been chipped off and there was corrosion on the spring coil surfaces in those regions. A sleeve was inside the spring. The brass guide spacer also was discolored. The adjustment nut locking mechanism was a drive pin through the nut and valve stem. There was rust on the nut and locking pin but there was no evidence of tampering.

Figure A-51. Appearance of PRV 270

When PRV 270 was disassembled the valve stem/poppet was loose from the valve body. There was a light interaction line on the valve stem but no corrosion. There were some stains on the surface of the valve stem in the region that was covered by the sleeve inside the spring. There was no evidence of gasket material stuck to the sealing surface of the valve body.

This examination has not revealed conclusive evidence for the high start-to-discharge pressure behavior for PRV 270.

PRV 351

PRV 351 is a ¾-inch, 250-psig set point valve produced by Manufacturer B. It had been in service for 12 years in a 172-gallon above-ground tank located in a rural environment described as warm and dry. A rain cap was not included with the valve. PRV 351 popped at a pressure of 336 psig (34-percent above its set pressure) during initial pressure testing. However, on subsequent pressure tests it opened and sealed at pressures between about 186 and 168 psig, respectively. This PRV was visually inspected and disassembled during the present study.

PRV 351 is shown in Figure A-52. It had a distinct rain cap line on the external surface. The internal surfaces of the valve body and the gasket holder were only slightly discolored and there was essentially no debris in the valve body.

The brass guide spacer was discolored and there was no washer between the guide spacer and the top of the spring; the spring was off center at that location, possibly indicating misalignment issues. The spring was bright and shiny and there was a sleeve inside the spring. As is shown in Figure A-52, the spring was bowed. The adjustment nut locking mechanism was a single nut, pinned from only one side. There was no evidence of tampering with the adjustment nut.

When PRV 351 was disassembled, the valve stem/poppet was stuck to the valve body. However, it broke loose when the rod was wiggled. There was no corrosion on the surface of the valve stem and only a light interaction line from contact between the guide spacer and the valve stem. In addition, there was no evidence of gasket material being stuck to the sealing surface of the valve body.

The examination of PRV 351 did not reveal any conclusive evidence to explain the high start-to-discharge pressure behavior.

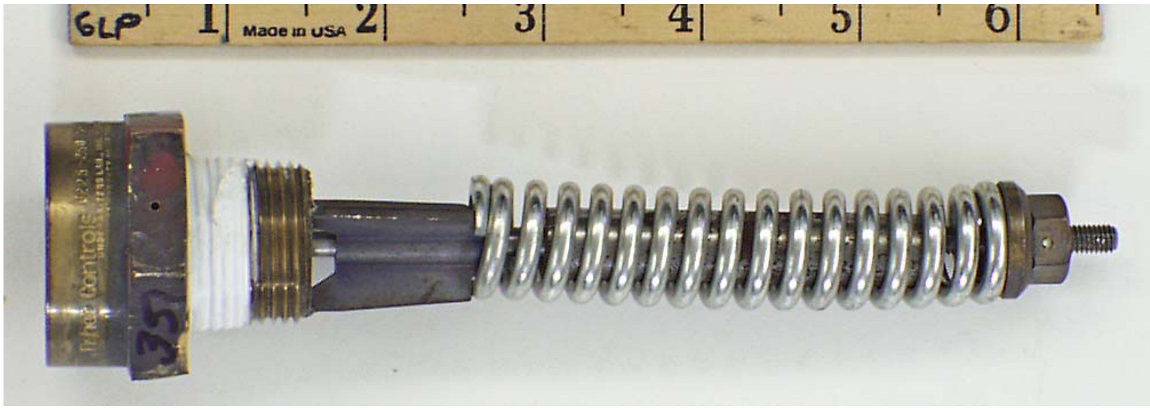


Figure A-52. Appearance of PRV 351

PRV 343

PRV 343 is a ¾-inch, 250-psig set point valve produced by Manufacturer B. It had been in service for 42 years in a 250-gallon above-ground tank, located in a rural environment described as cool and damp. A rain cap was not included with this PRV. During initial pressure testing, this valve opened at 327 psig, 31-percent above its set pressure. During a subsequent test it opened at 242 psig, which is below the valve set pressure.

PRV 343 is shown in Figure A-53. The black band at the top of the valve body indicates that a rain cap had been present. The internal surfaces of the valve body were discolored but there were no loose corrosion products or debris in the valve body. The valve body had three vertical tapered ribs protruding from the valve body. These ribs most likely aided in alignment of the poppet. The guide spacer had two legs and appeared to have been machined from bar stock. This is the only PRV examined that had that type of spacer. The surfaces of the spacer were discolored. The surfaces of the spring coils had a dull finish, but they were not corroded. The adjustment nut locking mechanism was a drive pin through the nut and valve stem. There was some corrosion on the nut and the threads of the valve stem extending beyond the nut, but there was no evidence of tampering.

When PRV 343 was disassembled, the valve stem/poppet was stuck to the valve body, but broke lose when the valve stem was wiggled. There was no corrosion or interaction line on the valve stem and no gasket material transferred to the sealing surface of the valve body.

The examination of PRV 343 has not revealed conclusive evidence to explain the high start-to-discharge pressure behavior.

Figure A-53. Appearance of PRV 343

PRV 132

PRV 132 is a ¾-inch, 250-psig set point valve produced by Manufacturer A. It had been in service for 13 years in a 250-gallon tank in an environment described as cool and dry. A rain cap was not included with this PRV. During initial pressure testing, PRV 132 opened at 325 psig, 30-percent above its set pressure. During a subsequent pressure cycles it opened at 159 psig and then it leaked on the third trial and would not seal.

PRV 132 is shown in Figure A-54. There was a distinct rain cap line on the external surface of the valve body. There was some discoloration on the internal surfaces of the body and the gasket holder, no loose corrosion products or debris in the valve body, and the weep hole was open. This PRV had a spacer fabricated from sheet steel into a slotted tube. Guide spacers were located at the top and bottom of the spring. The spring had a darkened, dull finish but there was no evidence of corrosion on the spring. A sleeve was present inside the spring. The adjustment/locking mechanism was a single nut with a single tack weld between the nut and the valve stem. There was some corrosion on the adjustment nut and the threads on the valve stem that extended beyond the nut. There was no evidence of tampering with the adjustment nut.

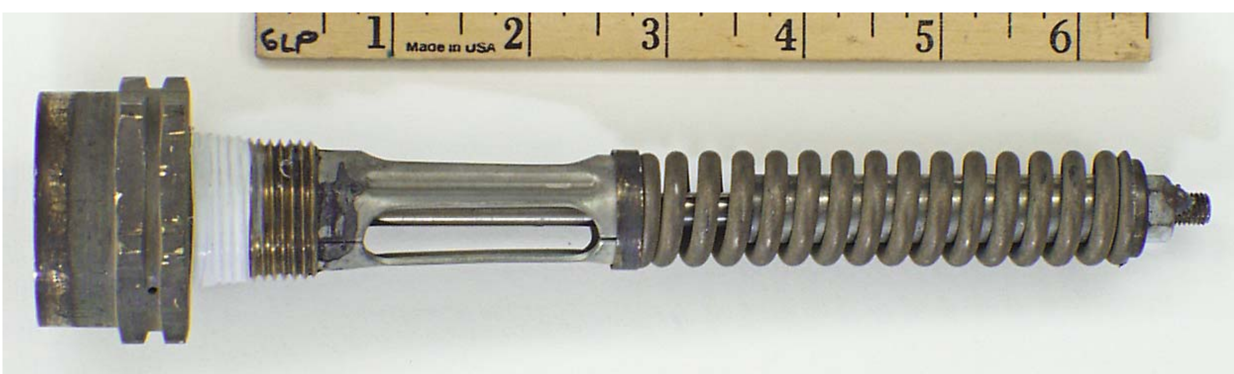


Figure A-54. Appearance of PRV 132

When PRV 132 was disassembled, the valve stem/poppet was loose from the valve body. There was no corrosion or interaction line from contact with the spacer guide on the valve stem. Also, there was no evidence of gasket material stuck to the sealing surface of the valve stem.

Examination of PRV 132 has not revealed evidence that can explain the high start-to-discharge pressure behavior.

PRV 268

PRV 268 is a one inch, 250-psig set point valve produced by Manufacturer D. It had been in service for 52 years in a 500-gallon tank located in a rural environment described as cool and damp. A rain cap was not included with this PRV. During initial pressure testing, PRV 268 opened at 368 psig, 47-percent greater than its set pressure. However, on subsequent pressure cycles, it opened at pressures between 214 and 218 psig and resealed at pressures between 205 and 208 psig.

PRV 268 is shown in Figure A-55. Examination of the valve body revealed no obvious external or internal rain cap line. The inside surfaces of the valve body and the surface of the gasket holder was discolored but there were no loose corrosion products or debris in the valve body. The weep hole was plugged with paint. There was an o-ring under the hex-shaped portion of the body that was covered with silver paint but it was not compressed. The spring was gold colored, bright and shiny. There was no evidence of corrosion on the spring. There was only a small amount of discoloration on the spacer. The components look very good for having been in service for 52 years. The adjustment nut locking mechanism was a single nut with a drive pin through the nut and valve stem. The hole on one side of the nut had been mis-drilled. There was some corrosion on the nut but there was no evidence of tampering.

Figure A-55. Appearance of PRV 268

When PRV 268 was disassembled, the valve stem/poppet was loose from the valve body. The valve stem had a somewhat dull finish, but there was no corrosion on its surface. There was an interaction line, not severe where the valve stem contacted the inner surface of the guide spacer. In addition there was no evidence of material transfer from the gasket to the surface of the valve body. Examination of PRV 268 has not provided evidence to explain the high start-to-discharge pressure behavior.

PRV 202

PRV 202 is a ¾-inch, 250-psig set point internal valve produced by Manufacturer A. It had been in service for 6 years in a 150-gallon above-ground tank that was located in a rural environment described as warm and damp. A rain cap was not included with this PRV. When PRV 202 was pressure tested, it opened at 362 psig, 45-percent above its set point pressure. It was not subjected to multiple pressure cycles.

PRV 202 is shown in Figure A-56. It had a distinct rain cap line on the external surface of the valve body. The remainder of that surface was discolored. The inner surfaces of the valve were not discolored and there was no debris in the valve body. There was another material, perhaps adhesive, on the external surface at the top of the spacer. Other than that, the components of the valve contained within the tank looked new. The spring had a shiny black coating and there was a sleeve inside the spring. The adjustment nut locking mechanism was a single tack weld between the nut and the valve stem.

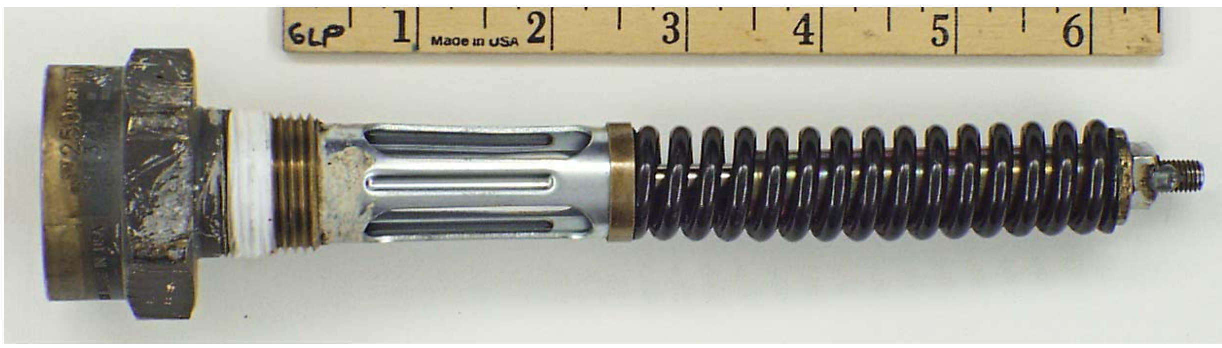


Figure A-56. Appearance of PRV 202

When PRV 202 was disassembled, the valve stem/poppet was loose from the valve body. There was no evidence of corrosion on the valve or any other components of the PRV. The valve stem was bright and shiny. Also, there was no gasket material stuck to the sealing surface of the valve body. This investigation has not provided evidence to explain the high start-to-discharge pressure behavior.

PRV 251

PRV 251 is a one inch, 250-psig set point internal valve produced by Manufacturer A. It had been in service for 53 years in a 500-gallon, above-ground tank in a rural environment described as cool and damp. A rain cap was not included with the PRV. When PRV 251 was initially pressure tested, it opened at 309 psig about 24-percent higher than its set point pressure. It was not subjected to multiple pressure cycles.

PRV 251 is shown in Figure A-57. Even though the external surface of the valve body was discolored, it appeared that a rain cap had been present. The internal surfaces of the valve body were discolored and there was debris in the valve body. The weep hole was plugged with paint.

The surfaces of the guide spacer showed a slight discoloration and the surfaces of the spring were gold colored, bright, and shiny; it looked new. There was a sleeve inside the spring. The adjustment nut locking mechanism was a drive pin through the nut and the valve stem. There was no rust present on the nut or the drive pin and there was no evidence of tampering.

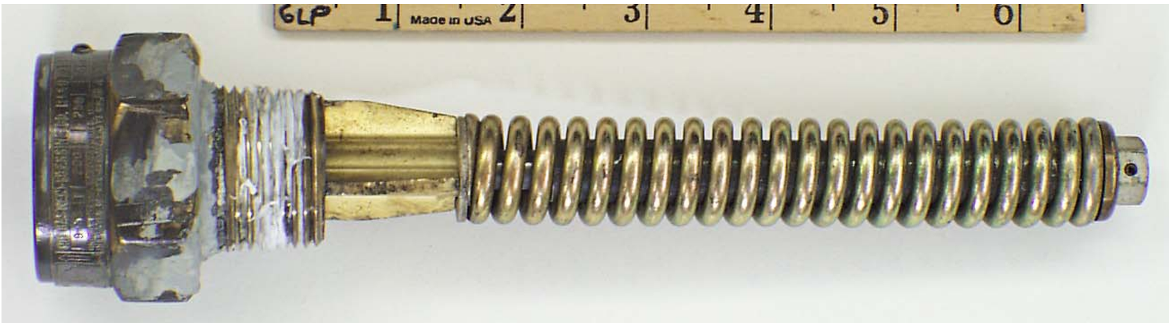


Figure A-57. Appearance of PRV 251

When PRV 251 was disassembled, the valve stem/poppet was stuck to the valve body, but it loosened when lightly wiggled. The valve stem had a dull metallic finish but there was no corrosion or an interaction from contact with the inner surfaces of the guide spacer. Also, there was no evidence of gasket material being stuck to the valve body. Again, no evidence was uncovered to explain the high start-to-discharge behavior of PRV 251.

PRV 19

PRV 19 is a ¾-inch, 285-psig set point, internal valve produced by Manufacturer B. It had been in service for 25 years in a climate described as warm and dry. The tank size and other location data were not reported. A rain cap was not provided with this PRV. The PRV opened at 348 psig, 39-percent above its set point, during initial pressure testing and 219 and 217 psig, about 27-percent below its set point, on subsequent pressure cycles. The PRV was inspected during the initial study and was re-examined during the present study. The examination during the initial study reported slight internal corrosion and deep compression set rings in the gasket [19].

During the present study, the overall condition of the components was verified. However, this examination revealed corrosion on the surface of the valve stem, as is shown in Figure A-58. Figure A-59 shows a higher magnification view of that corrosion and a faint interaction region from contact with the surfaces of the spacer guide. That amount of corrosion does not appear to be sufficient to cause the high start-to-discharge behavior.

Figure A-58. Corrosion on the Surface of the Valve Stem from PRV 19

Figure A-59. Higher Magnification View of the Corrosion and an Interaction Line on the Surface of the Valve Stem from PRV 19

The gasket material was Buna N and it had a Shore D hardness of 31, the same as a new gasket. It did not appear that there was pull out or material transfer from the gasket. The photograph of PRV 19 taken during the initial study showed that there was no washer between the brass spacer and the top of the spring. That feature was common to PRVs produced by Manufacturer B. However, in several of the other PRVs without the washer the spring was off center and/or bowed. That situation could indicate alignment issues with the valve stem and guides which could contribute to high start-to-discharge behavior when the PRV is pressurized.

PRV 41

PRV 41 is a one inch, 275-psig set point internal valve produced by Manufacturer A. It had been in service for 29 years in an environment described as warm and dry. The tank size and other location information were not reported. A rain cap was not included with the valve.

During the initial study, PRV 41 opened at 330 psig, 35-percent higher than its set point pressure on the first pressure cycle. It opened at pressures of 255 psig and 251 psig and sealed at pressures between 240 and 244 psig, essentially within set point tolerances on subsequent pressure cycles. It was examined and disassembled during the initial study and the valve components were re-examined during the present study.

As was described in the initial study and confirmed during the present study, the valve body was discolored but it appeared that there had been an internal rain plug. The spring had a black coating and much of it had flaked off. There was considerable surface rust where the coating was missing. The spacer also exhibited corrosion and guide washers at the top and bottom of the spring were discolored. The adjustment nut locking mechanism consisted of two nuts welded together. These nuts were easily removed and thus did not provide a tamper-proof mechanism, but there was no evidence of tampering. Some of the features described were illustrated in the report on the prior study [19].

The gasket showed cracks and material chipped from the outer edge and it was stuck in the holder. When the PRV was disassembled, the gasket was stuck to the valve body. However, it was released with light tapping.

The valve stem from PRV 41 is shown in Figure A-60. As is shown, there was not a lot of general corrosion on the surface but there was an extensive interaction region where the valve stem contacted the guide washer internal surface. This region is shown at higher magnification in Figure A-61. The amount of corrosion could have contributed significantly to the initial high start-to-discharge pressure behavior. The gasket from this PRV was identified as Buna N and exhibited a Shore D hardness of about 45. However, it is not known with certainty whether the material hardened during service.

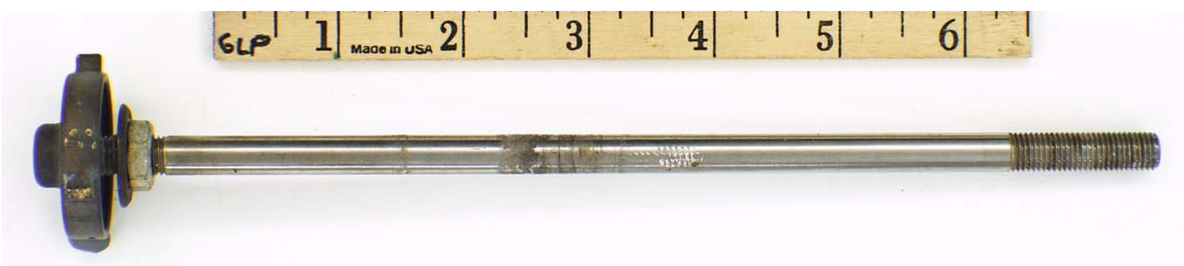


Figure A-60. Corrosion and an Interaction Region on the Surface of the Valve Stem from PRV 41

Figure A-61. Higher Magnification View of the Corrosion and the Interaction Region between the Valve Stem and the Guide Washer from PRV 41

Based upon the examination of PRV 41, it is likely that the high start-to-discharge behavior during initial pressure testing was caused by the valve stem being stuck to the guide spacer by the oxidation of the contacting surfaces. That condition can occur because of the condensation of moisture on the components inside the tank.

PRV 407

PRV 407 is a 250-psig set point, one-inch valve produced by Manufacturer A. It had been in service for 32 years in a 500-gallon, above-ground tank in a rural environment that was described as cool and dry. An internal rain/plug was included with PRV. This PRV was not tested during the initial program, but was tested during the present program using the original test procedure but with conditioning of the valve in a propane environment. The PRV opened at 329 psig, about 32-percent higher than its set point pressure. On subsequent pressurization cycles, it opened and resealed essentially within the set point pressure tolerance range.

The external surfaces of the valve body were discolored and had blotchy spots of white paint. The internal surfaces also were discolored but there was no loose debris in the valve body. The spring had a dull black coating and some of the coating had flaked off. Some light corrosion was present in the spring surface in those regions. There was no spacer inside the spring. The adjustment nut locking mechanism was two nuts tack welded together. That mechanism was not effective as the nuts were easily removed from the valve stem. However, there was no evidence of tampering with the adjustment nuts.

When PRV 407 was disassembled, the valve stem/poppet was loose from the valve body and there was no gasket material stuck to the sealing surface of the valve body. However, the gasket did exhibit radial cracks in the outer circumferential ring. Those cracks were shown previously in Figures 23 and 24. The valve stem has a dull metallic finish and an interaction line, not severe, similar to those observed on other PRVs. There was no corrosion on the valve stem.

As with most of the other PRVs that exhibited high start-to-discharge pressure behavior, no evidence that would explain this behavior was uncovered during the examination of PRV 407.