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January 6, 2012

Mr. Gregory Kerr
Propane Education & Research Council
1140 Connecticut Avenue N.W.
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Email: gregory.kerr@propanecouncil.org

Dear Greg,

FINAL REPORT ON "TESTING AND ANALYSIS OF THE PERFORMANCE OF PRESSURE RELIEF VALVES – NEW TEST PROTOCOL", PERC DOCKET 17071

Attached is an electronic copy of Battelle's final report for the project titled, "Testing and Analysis of the Performance of Pressure Relief Valves – New Test Protocol," PERC Docket Number 17071. The final report was split into two volumes. Volume I is the main body of the report including Appendices. Volume II contains photos for each PRV tested (top views, side views, and views of the information tags, if provided). Volume II has been split into 16 different PDF files.

If you have any questions or concerns, do not hesitate to contact me at (614) 424-3061.

Sincerely,

S. Flamberg

Stephanie Flamberg
Principal Research Scientist
Battelle – Energy, Environment, and Material Science

Attachments: Draft Report Volumes I and II.

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Testing and Analysis of the Performance of Pressure Relief Valves – New Test Protocol

Volume I – Final Report

Energy, Environment, and Material Sciences
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

To
Propane Education & Research Council
1140 Connecticut Avenue, NW, Suite 1075
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Battelle Project 100001707
PERC Docket 17071

December 2011

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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 (PRVs) 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 PRV samples for testing. In addition, we would also like to thank the PRV manufacturers and industry experts that provided valuable guidance on the test protocol and details on PRV manufacturing practices. This project would not have been a success without their assistance.

EXECUTIVE SUMMARY

In 2009, Battelle completed an experimental test program of pressure relief valves (PRVs) that had been removed from service to provide data to evaluate if the 10 to 15 year recommended service life for PRVs from several manufacturers could safely be extended. This program considered data from tests performed on nearly 400 PRVs removed from service, varying in age from less than 1 year to more than 60 years. The PRVs were 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.* The conclusion of that project was that although the test procedures outlined in UL 132 may be appropriate for new PRVs, they do not test to the conditions that PRVs experience in daily operation. As such, the results of this test program were inconclusive because the test protocol did not reflect the 'real-world' conditions that a PRV experiences in the field.

Using remaining project funds a modified test protocol was developed and evaluated to determine if test conditions more similar to field conditions affected PRV performance. The modified test protocol included conditioning the PRV in a propane environment, testing the PRV at a temperature representative of a hot day, and increasing the pressure to the PRV at a much slower rate (similar to a tank subjected to ambient heating). The conclusion of this exploratory testing was that a test protocol more representative of field conditions in which the PRV would be called to actuate did impact its performance.

The objective of the 2011 test program described herein is to expand upon the exploratory testing results using the modified test protocol. Because there is no performance standard for PRVs used in the field, the UL 132 start-to-discharge (STD) criteria for **new** PRVs was used as an indicator of performance. This does not infer that if a field-removed PRV performs outside the criteria for new PRVs it is not protecting the tank; rather it is an indicator of its performance against expectations for newly manufactured PRVs. For the remainder of the report the acronym NPC for "New Performance Criteria" is used when comparing the test results against the UL 132 STD criteria for newly manufactured PRVs.

A total of 325 PRVs were collected from field installations and a representative sample of 200 PRVs was tested under the modified test protocol. This study found that:

1. All but two PRVs tested opened within the maximum test pressure of 375 psig (1.5x a propane tank with 250-psig working pressure, equivalent to the hydrotest pressure). Both PRVs that did not open were 275-psig set pressure, over 30 years old, and identical PRVs from the same manufacturer.
2. A total of 102 PRVs had STD pressures within the NPC. These PRVs ranged in age from new to over 50 years old.
3. Beyond 15 to 20 years of age, there is a greater tendency for inconsistent PRV performance against the NPC. STD pressures ranged from 50 psig below the set pressure to 100 psig above the maximum set pressure (275 psig for 250-psig set pressure PRVs).

4. Statistically significant differences were noted for some manufacturers and some PRV sizes. The root cause could be age related differences in PRV groupings or an inherent design difference that affects the PRV performance under the test protocol.

Figure 1 and Figure 2 compare the STD pressures to the NPC and age for the 250-psi and 275-psi set pressure 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 set pressure, STD pressure, and full open pressure limits as specified in UL 132. The three different data symbols represent the pre-test visual inspection results (● = good; ▲ = marginal; X = poor). The darker gray band represents the range of acceptable PRV performance against the NPC. Data points with the label 'DNO' signify PRVs that did not open by 375 psi (1.5x the working pressure of a propane tank, equivalent to the hydrotest pressure). Significant differences between ages are evident by the variation in the vertical spread of the data points.

The test results show broad scatter in PRV performance against the NPC for PRVs older than 15 years of age for 250-psig set pressure PRVs and 30 years of age for 275-psig set pressure PRVs. The results also show that there are a higher percentage of PRVs older than 15 years receiving a 'marginal' or 'poor' visual inspection rating. Although high STD pressures begin to appear after 10 years, there does not appear to be a discernible trend of their percentage increasing with age until after 25 to 30 years of age (see Figure 3). The data suggests that PRV performance against the NPC may be influenced by PRV maintenance – PRVs that received 'marginal' or 'poor' visual inspection ratings tend to have STD pressures outside the bounds of the NPC.

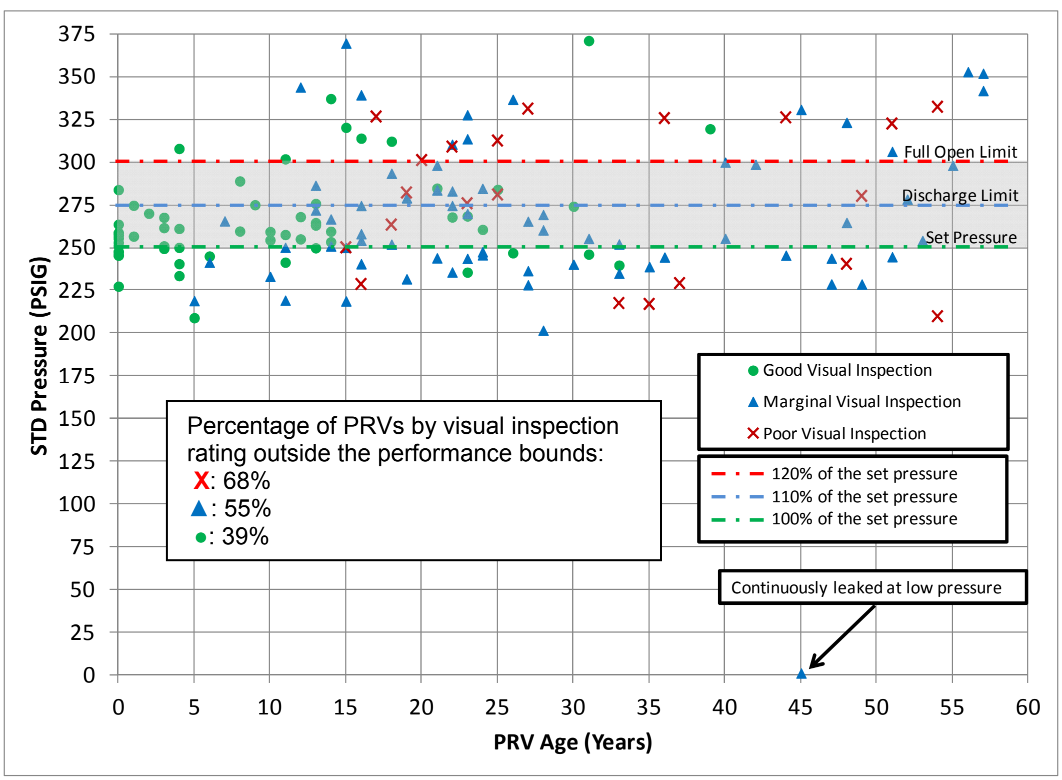

Figure 1. STD Pressure as a Function of Age, 250-psig Set Pressure PRVs

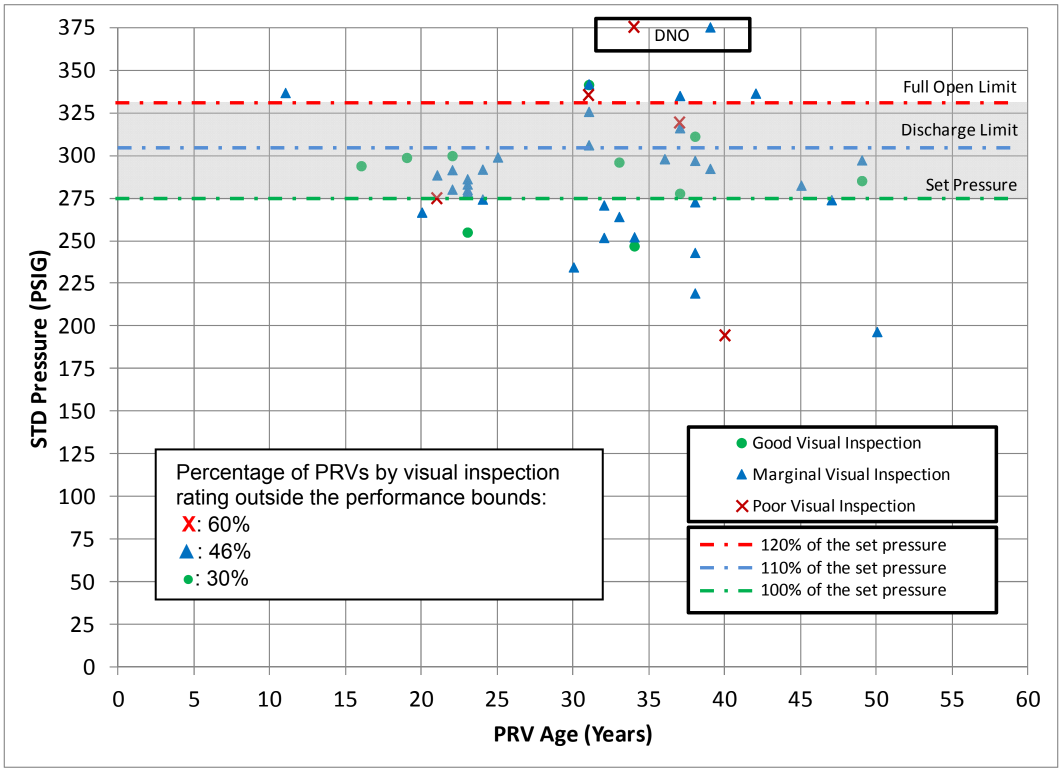

Figure 2. STD Pressure as a Function of Age, 275-psig Set Pressure PRVs

Statistical Analyses

Logistic regression models were developed to answer the following questions:

- Is there a tendency for PRVs to "stick" closed that depends on the age of the PRV?
- Is there a tendency for a PRV to open early (STD below the set pressure) that depends on the age of the PRV?
- Is there a tendency for a PRV to open late (STD >110 percent or >120 percent of the set pressure) that depends on the age of the PRV?

In statistics, logistic regression is used for prediction of the probability of occurrence of an event (sticking closed, opening too late, opening too soon, etc.) by fitting data to a logistic curve. P-values are then calculated to test the above statistical hypotheses. The p-value is the probability of obtaining a result as extreme or more extreme than what was actually observed, assuming that the null hypothesis is true (there is no performance difference due to the age of the PRV). The lower the p-value, the less likely the null hypothesis will be true so the more "significant" the result. The result of a test of significance is either "statistically significant" or "not statistically significant".

Significant p-values were only found for 250-psig set pressure PRVs opening late (STD>110 percent and STD >120 percent). The tendencies for a PRV to open early or to "stick" closed were found to be "not statistically significant." For the regression models that were statistically significant, plots were constructed to show the probability of performance as a function of PRV age. The plots contain estimates of the probability of opening greater than 120 percent of the set pressure by age, indicated by solid lines. This probability is based on the experimental data. A 95-percent upper confidence bound is indicated by the dashed line. This higher probability value factors in the limited amount of PRVs tested relative to the entire population installed and the variability observed in the test data.

PRVs that discharged late (>120 percent of the set pressure) were considered to have performance outside the bounds of the NPC. As shown in Figure 3, the probability for a PRV to discharge above this limit accelerates for PRVs older than 25 to 30 years of age as indicated by the increased slope of the line. The probability for new PRVs to open 120 percent above the set pressure can range from approximately 8 to 15 percent (with 95-percent confidence) increasing to 31 to 42 percent (with 95-percent confidence) for 40 year old PRVs. Note that these percentages refer to the response of the PRV to the applied pressure.[1]

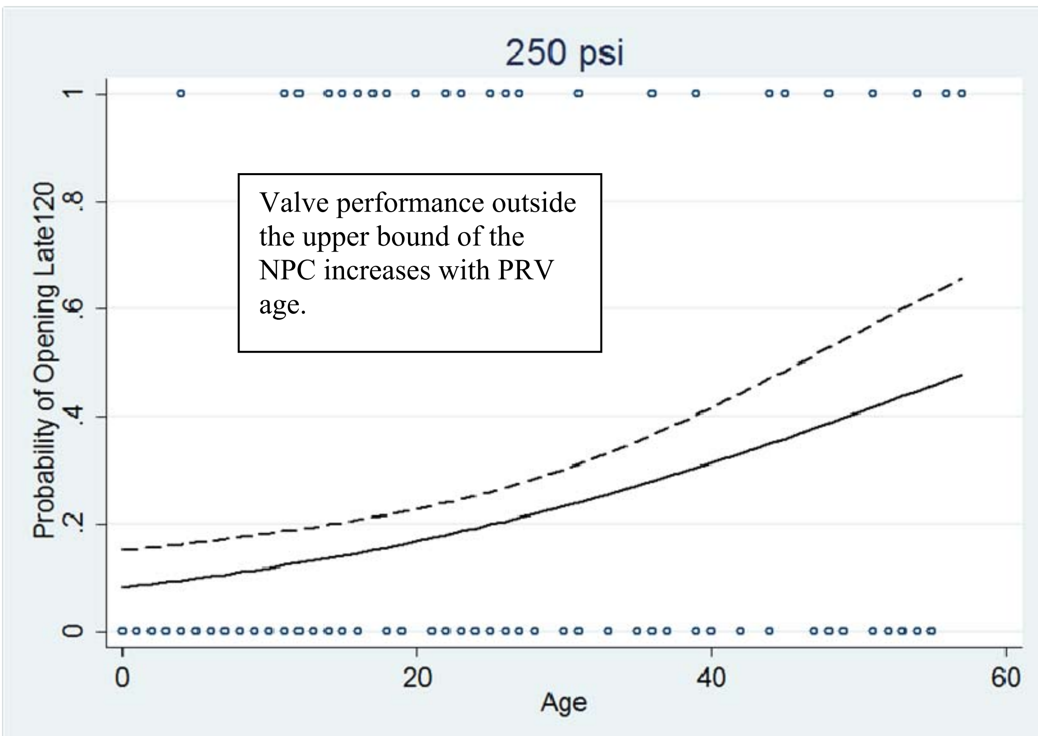

Figure 3. Probability for 250-psi Set Pressure PRV to Open Late (>120 percent of set pressure) vs. Age (years)

Forensic Analyses of Test PRVs

Battelle conducted a forensic analysis of selected PRVs that performed outside the bounds of the NPC to determine possible mechanisms and variables that may have contributed to the observed behavior. The examinations included observations of the conditions of the PRVs (visually and

[1] A tank pressure in excess of 300 psig (120 percent of 250-psig) is a lower probability field event that requires a combination of several external factors including a high tank fill level and unusually hot ambient weather conditions.

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 PRVs once disassembled. As the PRVs 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 two PRVs that were ‘stuck’ closed (did not open by 375 psig), 18 PRVs that exhibited high STD pressures (greater than 110 percent of the set pressure), and 4 PRVs that exhibited low STD pressures (less than the set pressure).

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 against the NPC (did not open, high STD or low STD) 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 4 (250-psig) and Figure 5 (275-psig). The numbers next to the symbols in the chart represent the PRV identification number.

Figure 4 and Figure 5 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 against the NPC.

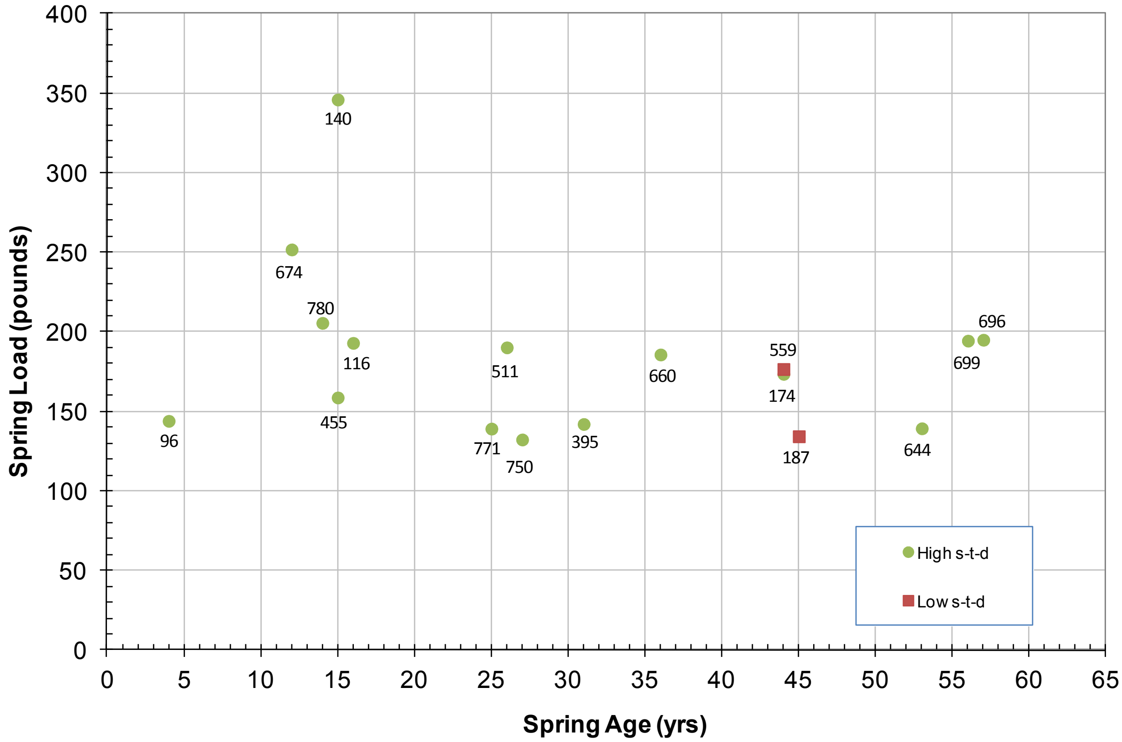

Figure 4. PRV Spring Load vs. Age – 250-psi Set Pressure PRVs

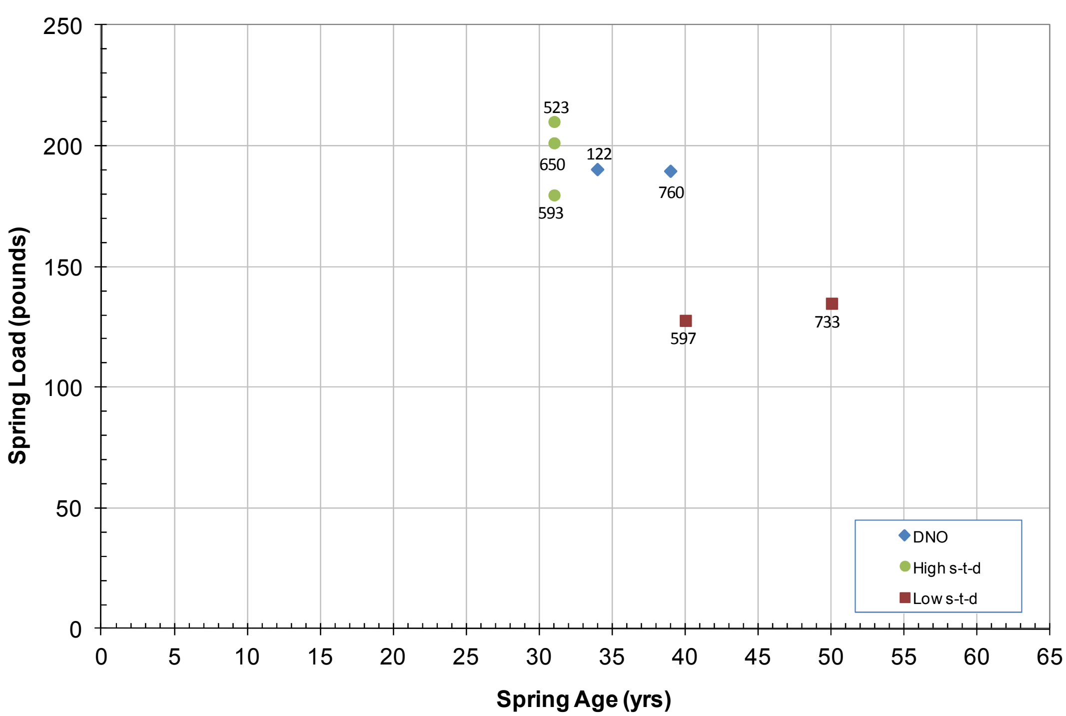

Figure 5. PRV Spring Load versus Age – 275-psi Set Pressure PRVs

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.

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

The hardness of the gaskets ranged from 16 to 64 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 STD, low STD) was plotted versus their age to see if there were general trends in their behavior over time (see Figure 6 and Figure 7). The data shows no strong trends or correlations.

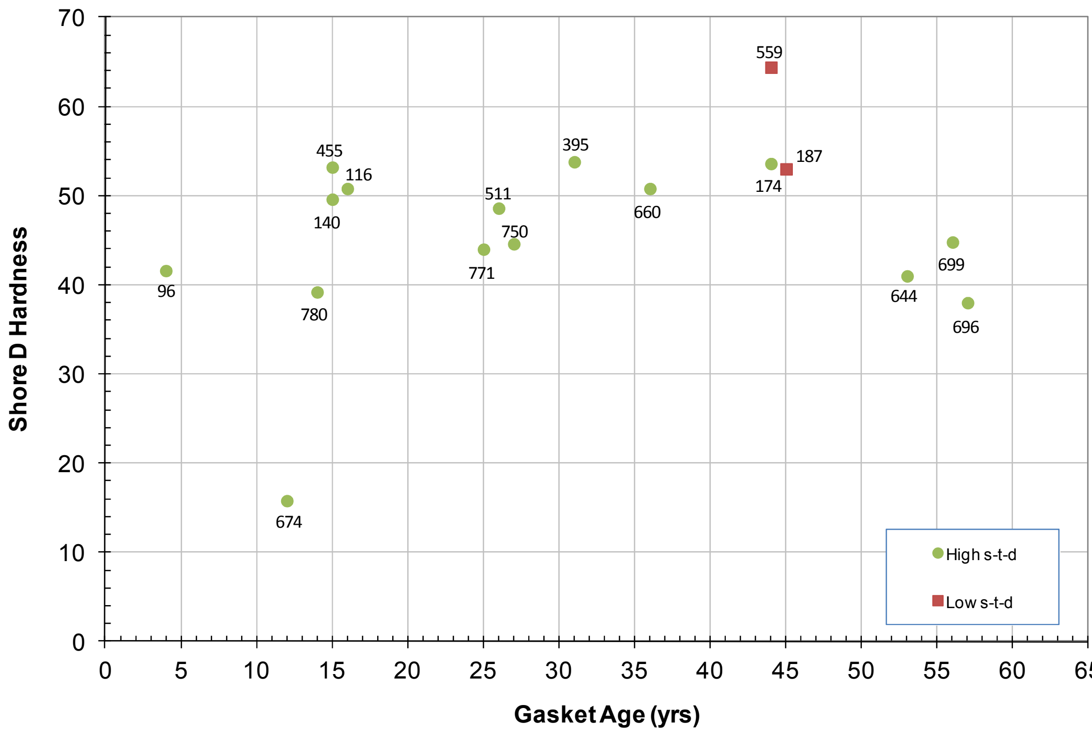

Figure 6. Gasket Hardness versus Age – 250-psi Set Pressure PRVs

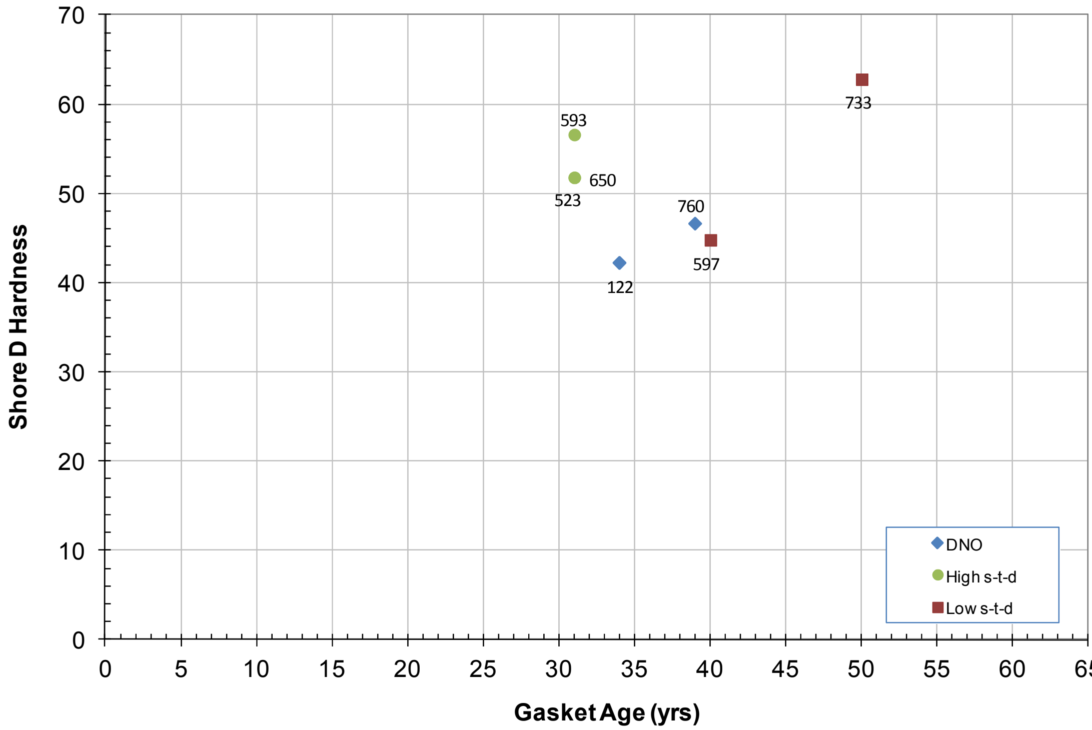

Figure 7. Gasket Hardness versus Age – 275-psi Set Pressure PRVs

Rain Cap Analyses

When the PRVs selected for examination were examined visually, it was observed that only two of 24 PRVs had rain caps included with the PRV. 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 PRV when shipped for the performance testing program. This analysis showed that about 67 percent (16 of 24) of the PRVs that were studied had evidence of a rain cap being present even though one may not have been included with the PRV provided for study. 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 PRV and help to keep weep holes clear.

Summary of Findings

Visual Inspections: All new PRVs were documented as 'good' condition for their visual inspection. The percentage of PRVs in 'good' condition slowly declines as the age of the PRV increases coincident with the rise of PRVs that received a 'marginal' rating for the visual inspection. The first 'poor' visual inspection ratings appear after 10 years of service. At ages in excess of 20 years the majority of PRVs receive a 'marginal' rating. Note that these ratings are an indication of the PRV condition based on observations of care and maintenance; they are not measures of actual PRV performance.

Manufacturers A, B, and C all had similar percentages of good, marginal, and poor ratings. The lack of good or poor ratings for Manufacturers D, E, F, and G are likely due to the relatively low number of PRVs in these categories (20 combined) rather than an inherently superior design, manufacturing process, or maintenance. The overall percentages of PRVs receiving good, marginal, and poor visual ratings did not have a strong correlation to connection size or set pressures.

PRVs that Did Not Open: Only 2 out of 200 PRVs tested (1 percent of the test population) did not open after reaching 375 psig. Both of these PRVs (PRV 122 and PRV 760) had 275-psi set pressures and the fact that they did not open was not found to be statistically significant (could have occurred by chance). Both PRVs were produced by Manufacturer C and are identical models. PRV 122 was 34 years old and PRV 760 was 39 years old. Examinations of these two PRVs showed many similar features, including stems that were difficult to remove from the PRV housing and severely corroded gasket holders. Based upon the examinations of PRV 122 and PRV 760, the Battelle investigators believe that the reason for the observed behavior was that the stems had become 'stuck' to the guide fittings during service even though significant corrosion did not occur between those surfaces.

PRVs that Exhibited High Start-to-Discharge Pressure Behavior: PRVs that discharged late (>120 percent of the set pressure) were considered to have performance outside the bounds of the NPC. Of the PRVs selected for forensic analysis, 15 of the 250-psig set pressure PRVs and 3 of the 275-psig set pressure PRVs exhibited high STD pressures against the NPC. All of these PRVs were examined visually and disassembled for more detailed examinations to determine to the extent possible the most probable cause for the high STD pressure behavior.

Examination of those PRVs revealed that most of them showed relatively little evidence of deterioration as a result of their service lives. The one high STD PRV that exhibited the most extensive corrosion on its exposed components was PRV 674 which had been in service for 53 years. This PRV was tested twice to 350 psig without opening; on the third pressurization cycle the PRV opened at 254 psig, very near the set pressure for the PRV. When the PRV was disassembled, the stem was stuck in the spacer guide and PRV housing. The stem was pushed out of the housing and spacer guide using an Instron universal testing machine. The load required to get measurable movement of the stem was 968.2 pounds (displacement was 0.015 inches). The load then dropped to between 500 and 600 pounds to move the stem. Based upon those measurements, it is difficult to understand how the PRV discharged at 254 psig during the third pressurization cycle. The Battelle investigators concluded that the high STD behavior of PRV 674 was caused by the corrosion of the stem and spacer fitting that was exposed to the environment inside the propane tank. This type of corrosion indicates that there was a significant amount of moisture inside the tank.

None of the other PRVs that exhibited high STD behavior during testing exhibited the extent of corrosion to their components as did PRV 674. However, all of them did exhibit a distinct mark on the PRV stem formed by contact between the PRV stem and the spacer guides. In addition, none of the PRVs exhibited evidence of sticking of the gaskets when they were disassembled. Consequently, the Battelle investigators concluded that the most likely reason for their high STD behavior was the sticking of the PRV stem to the guide spacers or guide washers.

When non-lubricated metallic materials are in intimate contact under essentially static loads, they will stick together because of slight oxidation of the surfaces even though significant corrosion does not occur. This behavior suggests that the use of solid film lubricants or CPCs (corrosion prevention compounds) might be highly beneficial to improve PRV performance.

PRVs that Exhibited Low Start-to-Discharge Pressure Behavior: Of the PRVs selected for forensic analysis, four PRVs exhibited low STD pressure behavior against the NPC. PRV 559 leaked at the small ring gasket used as the seal between the head of the stem and the gasket holder.

The internal components of PRV 187 were extremely rusty. Most of the rust on the surface of the PRV stem, the spring, the spacer inside the spring, the housing, and the gasket holder appeared to have been deposited on those surfaces rather than formed by corrosion of the surfaces. It was as if this PRV was exposed to rusty water after removal from the tank. There did not appear to be a continuous path of rust across the sealing surface of the gasket. Consequently, there is no conclusive evidence to indicate why this PRV leaked around the gasket during testing.

PRV 597 appeared to be in relatively good condition; however, there was a dent in the machined surface of the housing that also imprinted on the gasket. These features were the only deficiencies observed and they do not appear to be the reason for the low STD pressure behavior. Based upon this examination there is no conclusive evidence for the low STD pressure behavior.

PRV 733 also appeared to be in relatively good condition. The spacer was discolored and some of the coating had chipped off the spring but there was no significant corrosion. PRV 733 did have a crack in the sealing surface of the gasket. It is possible that this crack caused the low STD pressure behavior of this PRV. Also, the average hardness of the gasket was 63 Shore D, the second highest hardness measured on the gaskets.

Summary: All tested 250-psig set pressure PRVs opened by 150 percent of the working pressure (375 psig). Only two 275-psig set pressure PRVs did not open by 375-psig[2] and it is believed that the observed behavior was due to the PRV stems becoming ‘stuck’ to the spacer guides during service even though significant corrosion did not occur between those surfaces.

For PRVs that did open, the STD pressure exhibited a high amount of variability. A considerable population did not open within the NPC of 100 percent to 120 percent of the set pressure (98 PRVs). Small differences were observed based on various breakdowns including size, manufacturer, and age but none of the breakdowns distinguished themselves as particularly good or bad. The most likely reason for their high STD behavior was the sticking of the PRV stem to the spacer guides or guide washers except for PRV 674 which showed extensive corrosion on several PRV components that likely caused the high STD.

Age still appears to be the single most significant factor affecting PRV performance. The forensic analyses indicated that sticking of the PRV stem to the guide spacers or guide washers was the most likely cause for the high STD pressures and PRVs not opening during testing. Additionally, the corrosion found on some of the internal components of the PRVs examined is suspected to have come from high moisture in the propane. Moreover, older PRVs are more

[2] Note that the maximum test pressure of 375 psig is less than 150 percent of the PRV set pressure and it therefore is not conclusive that these PRVs would not have opened before the hydrotest pressure of tanks with a design working pressure of 275 psig on which they were installed.

susceptible to a build-up of dirt/debris within the PRV especially if the rain cap has been removed. This dirt/debris can plug the weep hole and allow water to collect in the PRV body. As such, maintenance (checking rain caps and weep holes) may be just as important as the age of the PRV.

An additional factor is the knowledge that PRV manufacturers intentionally set higher PRV set pressure tolerances to meet both UL 132 and ASME Section VIII requirements. This was due to the California Title 8 requirement that only ASME rated PRVs could be used on ASME containers. Since California's adoption of the 1998 version of NPFA 58, UL PRVs can now be used without a California setting. Several of the California setting PRVs shows higher STD pressures. Nineteen of the twenty-eight California setting PRVs had STD pressures over 275 psig (110 percent of 250 psig). Only 9 California setting PRVs had STD pressures over 312.5 psig (110 percent of 275 psig). The remaining California setting PRVs (9 of the 28) had STD pressures between 230 and 275 psig. These higher initial set pressure tolerances are likely contributing to the statistically significant higher STD pressures for older PRVs.

Based on the observed data, it is unlikely that testing a larger number of PRVs would affect the outcomes of this performance test program. While small shifts in the probability of a PRV opening may be realized, the data will likely still indicate that a majority of the PRVs will open by 150 percent of the tank working pressure with a substantial portion of that population having an STD pressure outside the NPC.

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Terms and Acronyms

ASME	American Society of Mechanical Engineers
DAQ	Data Acquisition
EDS	Energy Dispersive Spectroscopy
FT-IR	Fourier Transform-Infrared
hr	hour
lbs	pounds
LPG	Liquefied petroleum gas
NPC	New Performance Criteria
NPGA	National Propane Gas Association
PC	Personal Computer
PERC	Propane Education & Research Council
PID	Proportional, Integral, Derivative
PRV	Pressure Relief Valve
psig	pound per square inch gauge
RDAC	Research & Development Advisory Committee
STD	Start-to-Discharge
UL	Underwriters Laboratories
W	Watt

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1.0 Program Objectives and Introduction

Pressure relief valves (PRVs) are used to protect propane containers from over-pressurization. Excessive pressure can occur as a result of an increase in temperature experienced during a fire or because of ambient heating coupled with an overfill of the tank. PRVs are typically spring-loaded devices intended to prevent the internal container pressure from rising above a predetermined maximum by venting the excess pressure and then resealing when the pressure is reduced to an acceptable level.

Currently, major manufacturers of PRVs for use with propane containers recommend that the PRVs be replaced every 10 to 15 years with caveats related to shortening of the PRV's useful life due to environmental conditions, inspections, and/or maintenance programs. The propane marketer must then observe and determine the appropriate replacement interval for PRVs in their territory.

Recently, the California Department of Industrial Relations has considered the enforcement of manufacturers' recommendations as requirements for replacing PRVs on tertiary consumer propane tanks. Because the documented number of PRV failures causing tank rupture in service is minimal, and the service life observed in the field is typically more than 10 years, these regulations could result in significant, unnecessary maintenance impacts and safety issues to the propane industry and consumers. This report intends to provide the Propane Education & Research Council (PERC) with technical data that can be used as a basis for discussion in answering questions regarding the service life of PRVs on the market.

In 2009, Battelle completed an experimental test program of PRVs that had been removed from service to provide data to evaluate if the 10 to 15 year recommended service life for PRVs from several manufacturers could safely be extended. That program considered data from tests performed on nearly 400 PRVs removed from service, varying in age from less than 1 year to more than 60 years. The sample of PRVs was tested to a protocol that was developed from Section 11, Test No. 1 of Underwriters Laboratory (UL) Standard 132, *Safety Relief Valves for Anhydrous Ammonia and LP-Gas*. The conclusion of that project was that although the test procedures outlined in UL 132 may be appropriate for new PRVs, they do not test to the conditions that PRVs experience in daily operation. Therefore, the results of the test program did not accurately represent the 'real-world' conditions that a PRV experiences in daily operation.

Using remaining project funds a modified test protocol was developed and evaluated to determine if test conditions more similar to field conditions affected PRV performance. The modified test protocol included conditioning the PRV in a propane environment, testing the PRV at a temperature representative of a hot day, and increasing the pressure to the PRV at a much slower rate (similar to a tank subjected to ambient heating). The conclusion of this exploratory testing was that a test protocol more representative of field conditions in which the PRV would be called to actuate did impact its performance.

The objective of the 2011 test program described herein is to expand upon the exploratory testing results using the modified test protocol. Volume I of this report summarizes the results of the test program. Photographic documentation of the PRVs is provided in Volume II of this report.

Figure 8 contains a high level flowchart of the modified test protocol. A number of used PRVs were collected from propane marketers for use as the test samples. Information pertaining to the PRV's physical and usage attributes was recorded in a database. From the entire collection, a statistically significant sample of PRVs was selected for testing. The modified test protocol applied included the following steps:

1. Install the PRV in a conditioning apparatus and fill with propane. The propane was commercially available propane obtained from a local marketer.
2. Maintain propane conditioning for at least seven days.
3. Install the PRV on the STD test rig and heat to 130°F.
4. Slowly increase pressure at a rate of +0.24 psig/minute until flow is measured, indicating the PRV has opened.

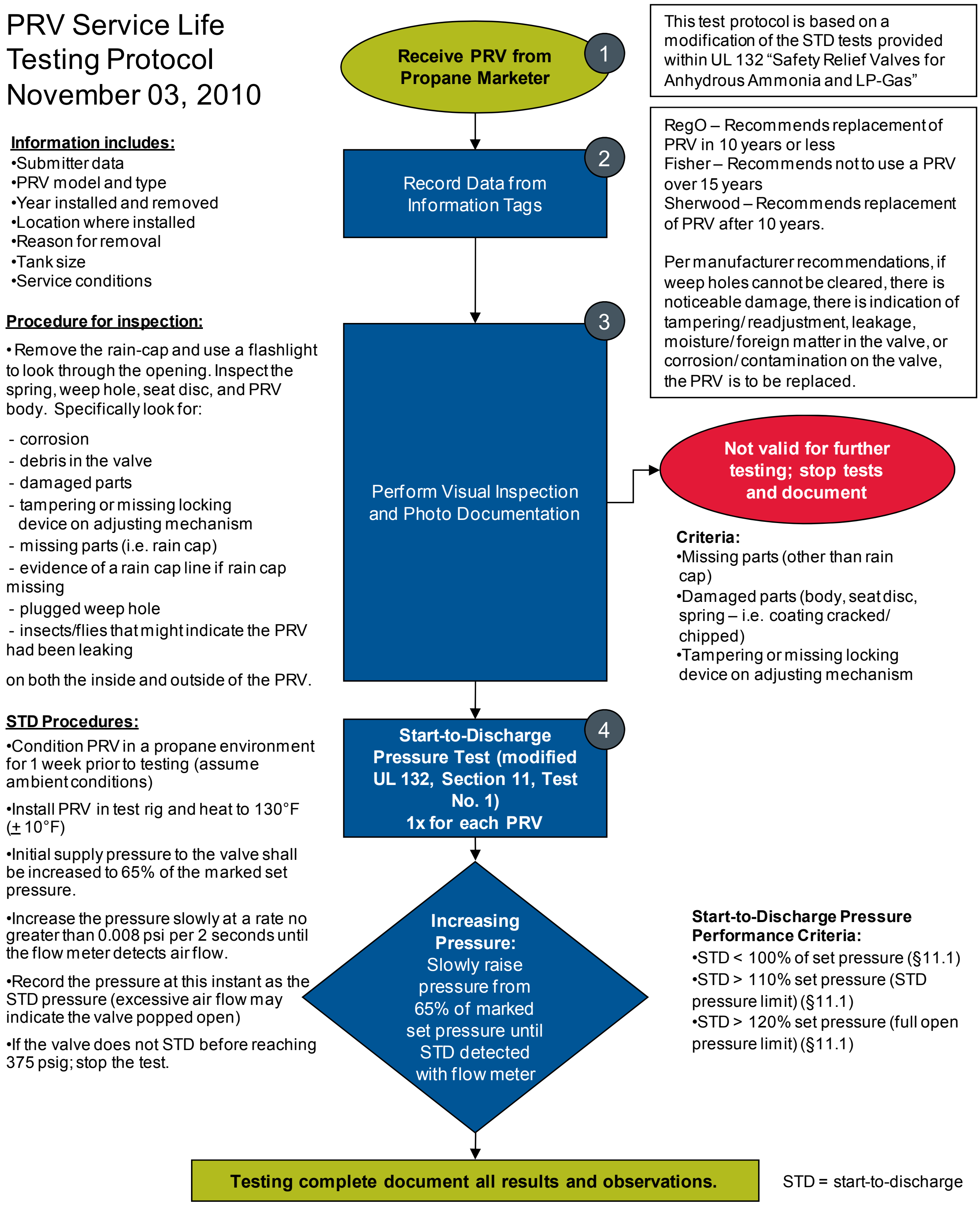

Figure 8. Collection and Test Protocol

2.0 PRV Sample Collection and Inspection

The objective of this project was to subject a large set of PRVs representing a variety of ages, sizes, manufacturers, and service conditions to a test representative of real world conditions in which the PRV would be called to relieve pressure and investigate the scientific merit behind PRV replacement guidelines. A total of 200 PRVs were to be tested in this project. A larger sample of PRVs was collected by Battelle so that a subset that ensures a diverse representation of age, size, and manufacturer could be selected for testing.

2.1 PRV Acquisition

Battelle targeted having a minimum of 300 PRVs from which the test matrix of 200 PRVs could be selected. Upon completion of the 2009 PRV project, Battelle retained 52 PRVs that were collected but not tested[3]. To facilitate a larger, more diverse representation of PRVs, those PRVs were included in the current PRV selection matrix.

Battelle worked with the NPGA, PERC, and industry members to collect an additional 249 PRVs from propane marketers located throughout the United States and Canada. Battelle also purchased 24 new PRVs. Combined with the 52 PRVs remaining from the 2009 project, the total selection pool available for testing was 325 PRVs.

The additional PRVs were submitted by 25 different propane marketers in response to email requests and a letter of solicitation sent by Battelle (Appendix A). The request asked for PRVs recently removed from service (within the past month) for any reason other than malfunction. Marketers interested in submitting PRVs to Battelle were provided shipping supplies and information tags for the PRVs. Marketers were asked to supply as much of the following information on the information tag as possible.

- Submittal Date
- Contact Information
- PRV Manufacturer
- Model Number
- PRV Set Pressure
- Container Connection Size
- Year Installed
- Date Removed from Service (must be within the past month)
- PRV Location
- Geographic Service Area
- Reason for PRV Removal
- General Operating Conditions (location at tank; location at building; tank size)

The collection effort specifically targeted PRVs used on ASME tanks to examine the assumptions behind the 10- to 15-year replacement recommendations. Since external PRVs are no longer being used for these applications, only internal spring PRVs were requested and tested.

[3] A total of 100 untested PRVs remained from the 2009 test program. Forty-eight PRVs were inadvertently disposed when transferring the PRVs from the laboratory test area to long term storage.

Upon receipt of the PRVs at Battelle, they were cataloged in a Microsoft Excel Spreadsheet. The spreadsheet has several detailed fields that include all the information on the submittal tags. The submittal information is verified and/or supplemented with information stamped on the PRV.

2.2 PRV Visual Inspection and Photographic Documentation

Following the entry of PRVs into the catalog spreadsheet, each PRV was subjected to a visual inspection. The inspection results were logged in a Microsoft Access database. The user interface to the database is shown in Figure 9. The data entry form provides a consistent means of ensuring each PRV is inspected for the same criteria and with the same attention to detail. As can be seen in Figure 9, various sections of the form focus on the exposed (external to the tank) PRV components and the internal (to the tank) PRV components. The visual inspection included the following checks:

- Corrosion (external or internal)
- Dirt/debris in the PRV
- Damaged parts
- Missing parts (including the rain cap)
- Tampered or missing locking device on adjusting mechanism
- Plugged weep hole
- General observations

Comment fields were provided to allow for clarification or notation of any observations.

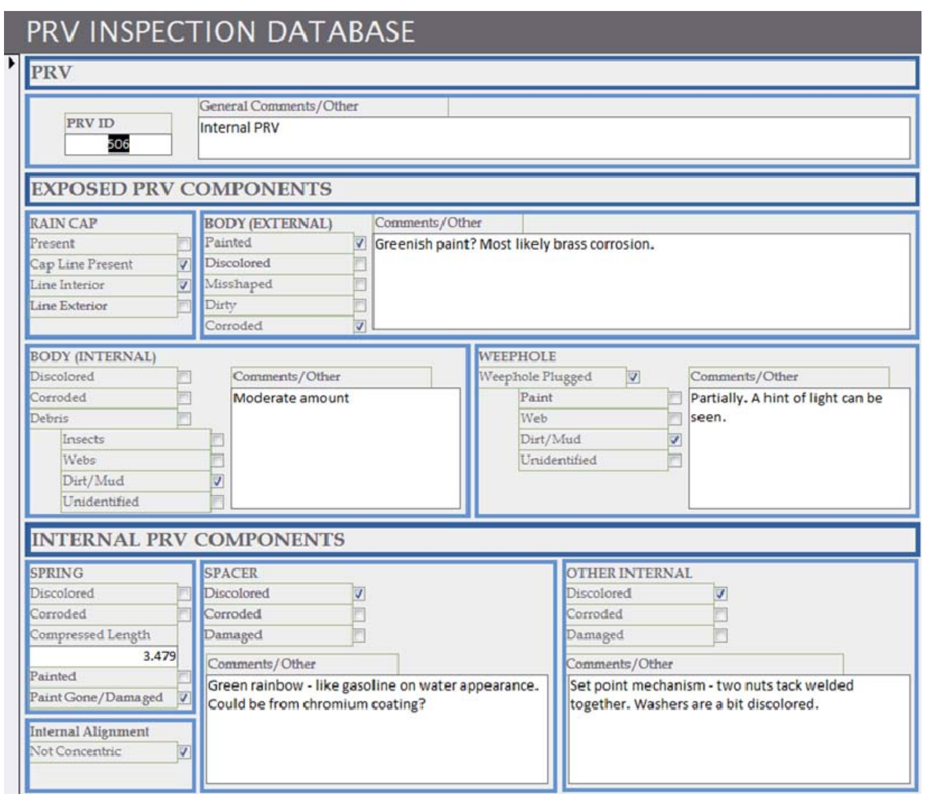

Figure 9. PRV Inspection Database User Interface

Photographs of each PRV were collected upon completion of the visual inspection. An example of the photographs collected is shown in Figure 10. Combined with the visual inspection, these efforts document the "as received" condition of each PRV. The documentation also creates a reference point for future enquiries about the received condition of the PRV for both the current and possible future considerations.

Figure 10. Representative Photos Collected for Each PRV

Rating criteria were established to assess the condition of the PRV. Three inspection ratings were given: Good, Marginal, and Poor. The basic intent of the rating is to assess overall PRV condition and indications of adherence to manufacturer recommendations for proper usage and maintenance. Per manufacturer recommendations, the PRV is to be replaced if the weep hole cannot be cleared, there is indication of tampering or readjustment of the set pressure, or there is observed damage to the body, seat leakage, moisture/foreign matter in the PRV, or corrosion/contamination in the PRV. PRVs that were found to be corroded, missing the rain cap, damaged, and/or had an accumulation of dirt/debris were documented as 'poor' or 'marginal' but were still tested to determine their performance against the NPC.

The visual inspection grading criteria are detailed in Figure 11 and further described below.

- Poor
  - Severe mechanical damage to the PRV was observed.
  - Alternatively, if the weep hole was plugged by webs, dirt, or other debris a 'poor' rating was assigned since manufacturer recommendations include clearing weep holes.
- Marginal
  - Some corrosion or minor mechanical damage to the PRV may have been observed. As the spacer often exhibits some corrosion, corrosion of the spacer alone was insufficient to meet the 'marginal' rating criteria.
  - PRVs that lacked a rain cap or rain cap line were rated as 'marginal' as well. While it is common for the rain cap to become lost or separated during removal and transport of the PRV, the lack of either the cap or the line (indicating it had been present for at least a significant portion of the PRV field life) would indicate the PRV was likely susceptible to accumulating moisture/foreign matter in the PRV (including plugging the weep hole).
  - A 'marginal' rating was also given to PRVs with weep holes plugged by paint.
- Good
  - A good rating was assigned to PRVs that appeared in good overall condition and exhibited reasonable evidence of proper maintenance. This includes minimal corrosion, the presence of a rain cap or rain cap line, and a partially to fully clear weep hole.

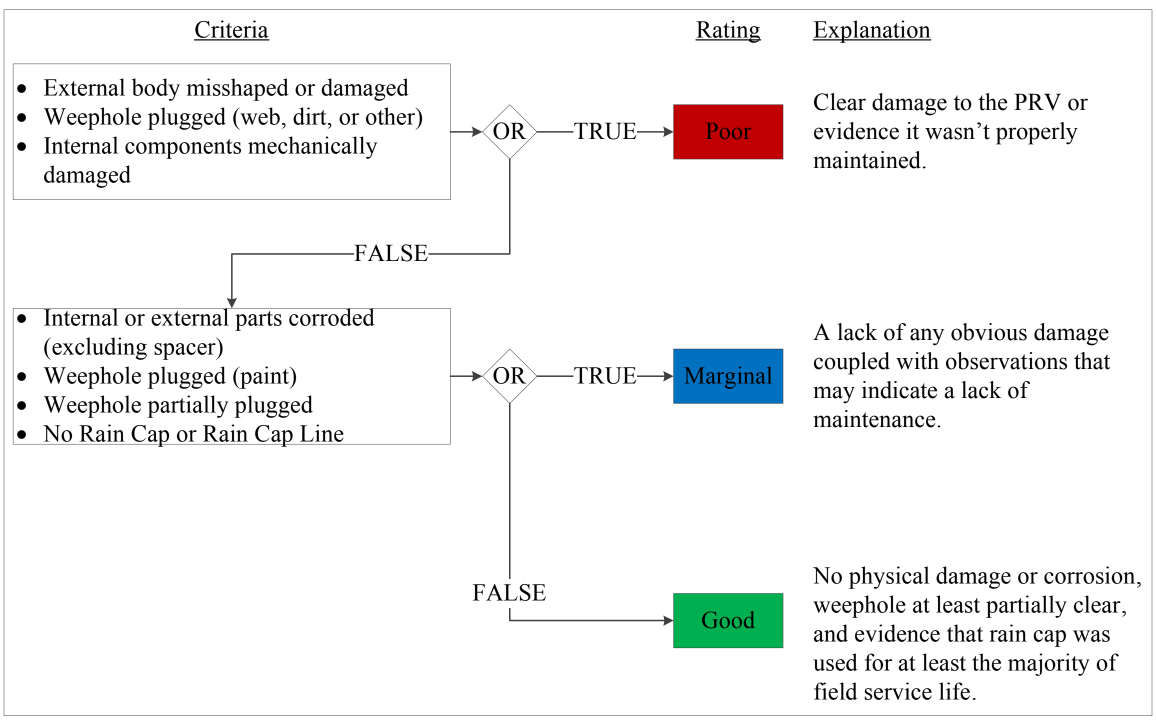

Figure 11. PRV Visual Inspection Logic Diagram

Using the criteria in Figure 11 ratings were assigned to each PRV. When necessary, the photographs of the PRVs were examined to clarify results or comments in the inspection database. The breakdowns of the 200 tested PRVs for a number of metrics are shown in Figure 12 (Age), Figure 13 (Manufacturer), Figure 14 (Connection Size), and Figure 15 (Set Pressure).

Figure 12 shows the expected degradation of PRV condition with age. All new PRVs were documented as 'good' condition for their visual inspection. The percentage of PRVs in 'good' condition slowly declines as the age of the PRV increases coincident with the rise of PRVs that received a 'marginal' rating for the visual inspection. The first 'poor' visual inspection ratings appear after 10 years of service. Note that these ratings are an indication of the PRV condition based on observations of care and maintenance; they are not measures of actual PRV performance.

Figure 13 shows the breakdown of PRV ratings by manufacturer. Manufacturers A, B, and C all had similar percentages of good, marginal, and poor ratings. The lack of good or poor ratings for Manufacturers D, E, F, and G are likely due to the relatively low number of PRVs in these categories (20 combined) rather than an inherently superior design, manufacturing process, or maintenance.

The overall percentages of PRVs receiving good, marginal, and poor visual ratings did not have a strong correlation to connection size or set pressures, as shown in Figure 14 and Figure 15. Note that in Figure 15 while the percentage of 'good' ratings 275-psig set pressure PRVs is considerably lower than for 250-psig set pressure PRVs, this is likely due to the relative age of the PRV samples. Only three of 50 tested 275-psig PRVs had an age less than 20 years while 77 of the 150 tested 250-psig PRVs had an age less than 20 years. As shown in Figure 12, at ages in excess of 20 years the majority of PRVs receive a 'marginal' rating.

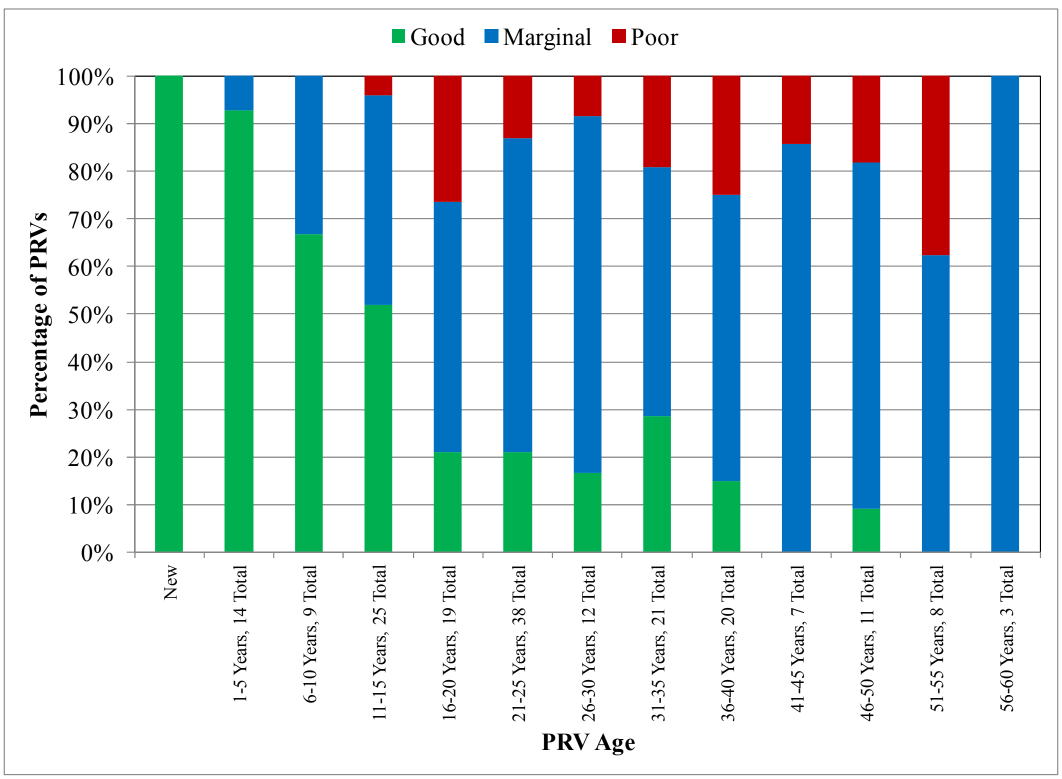

Figure 12. PRV Visual Inspection Ratings by Age

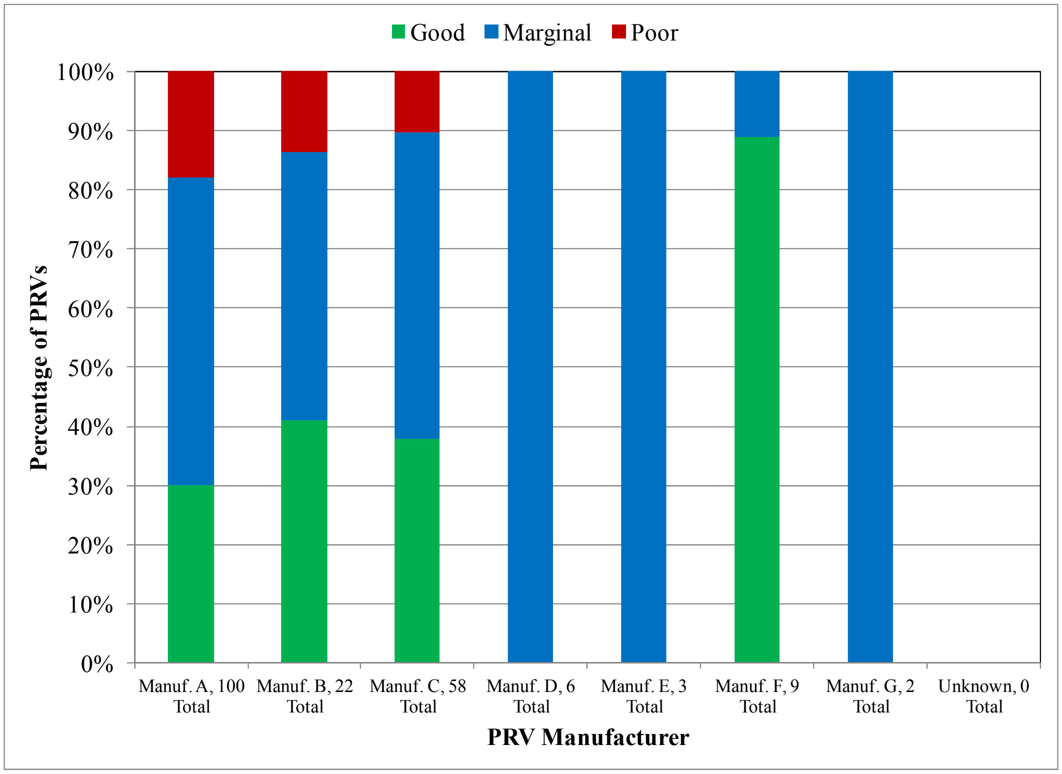

Figure 13. PRV Inspection Ratings by Manufacturer

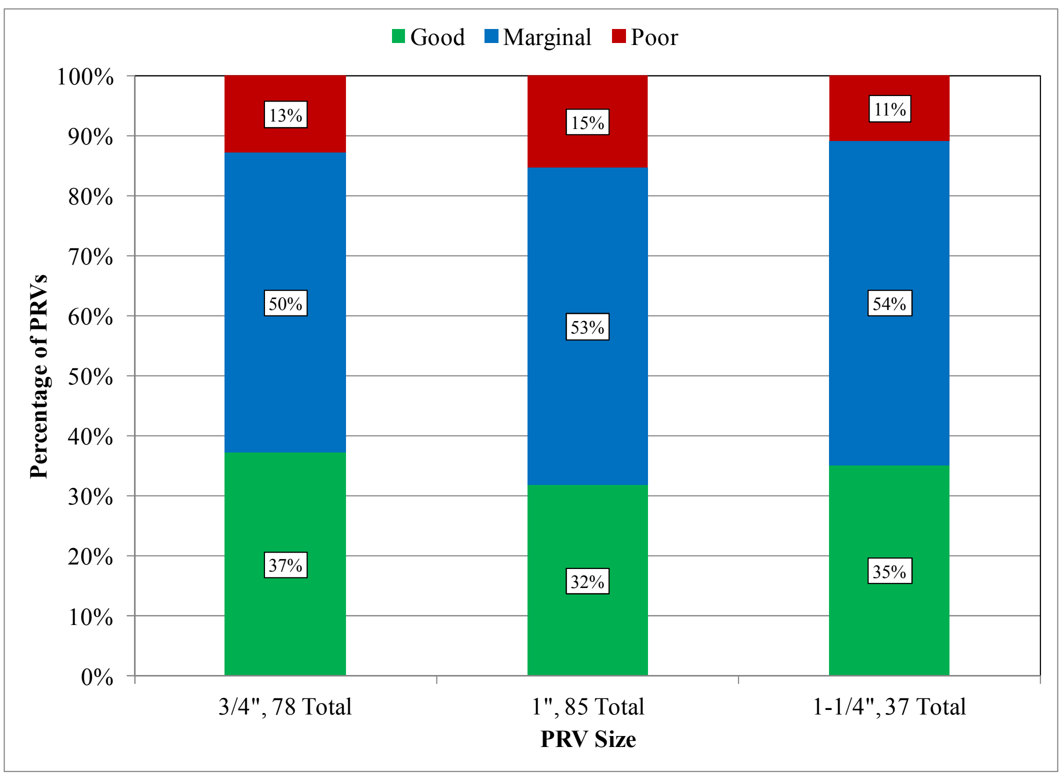

Figure 14. PRV Inspection Ratings by Connection Size

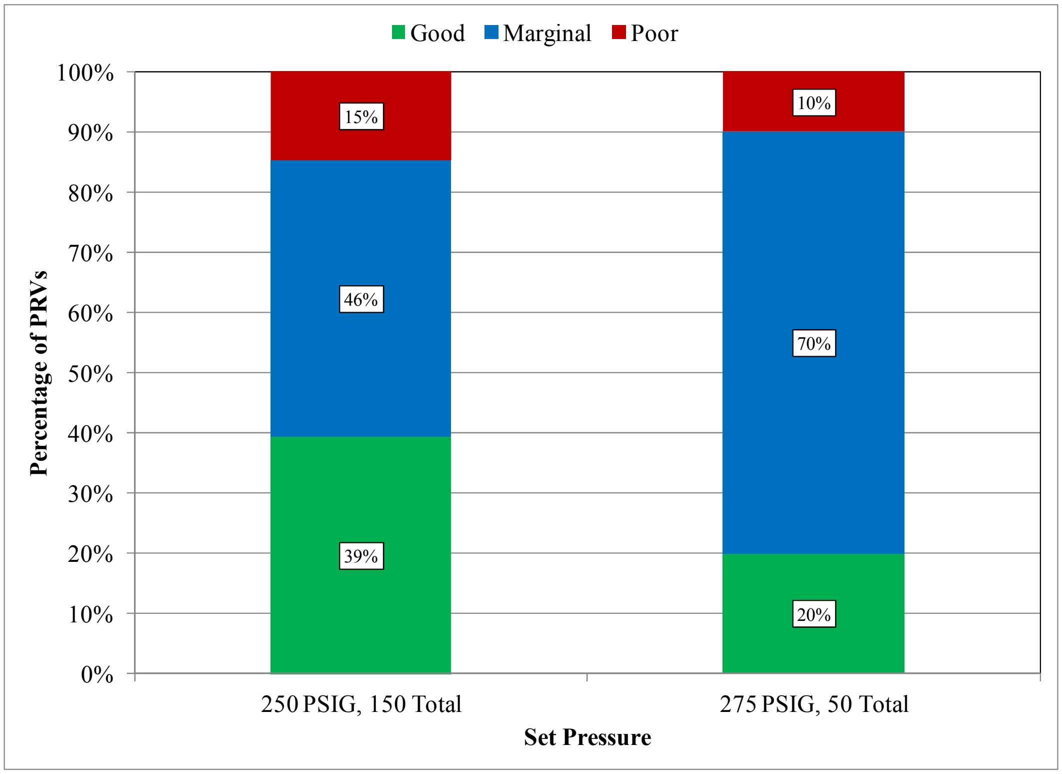

Figure 15. PRV Inspection Ratings by Set Pressure

2.3 PRV Selection for Testing

A total of 25 propane distributors responded to the letter of solicitation. Their submittals, coupled with remaining PRVs from the previous test effort, created a pool of 325 PRVs from which the test matrix could be selected.

Twenty PRVs submitted for the test program were the external type (five previously collected and fifteen from the current collection). As this project is focused solely on internal spring type PRVs[4], the twenty external PRVs were excluded from the samples selected for testing. The breakdown of PRVs by type is shown in Figure 16.

[4] Most propane tanks in residential and commercial service use internal spring PRVs because they present less of an obstruction. External PRVs are found primarily on older tanks and are generally replaced with internal spring PRVs during tank maintenance or refurbishment.

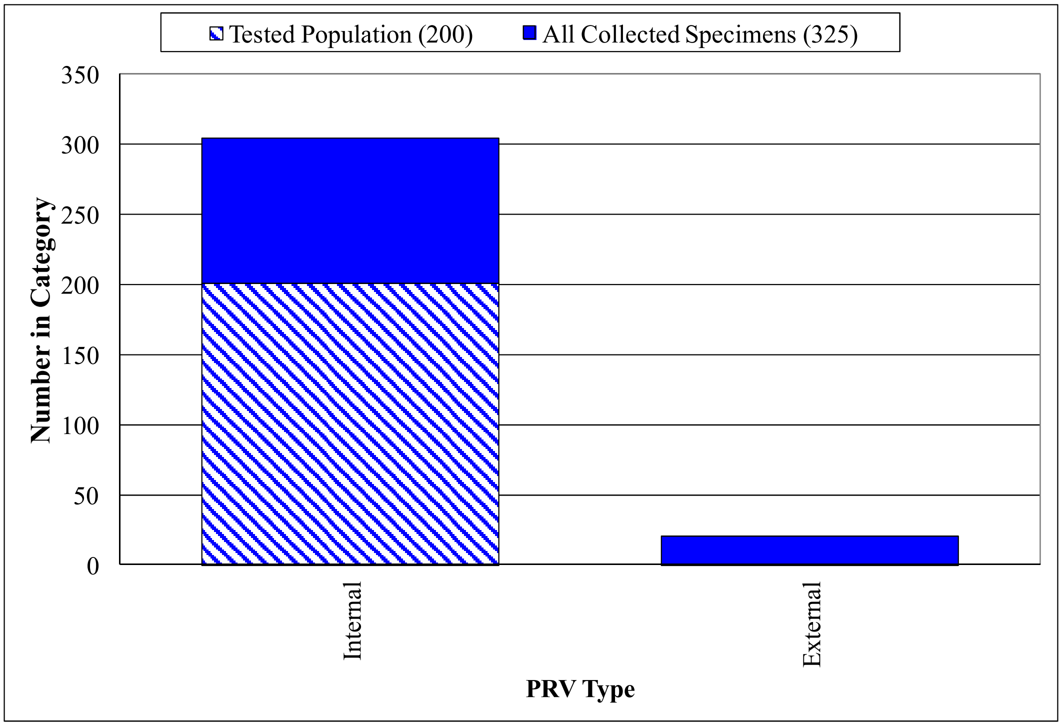

Figure 16. PRV Test Matrix Breakdown by Type (Internal/External)

After excluding external type PRVs, the test matrix of 200 PRVs was sampled to ensure that the test population was proportionally representative of the collected PRV population for factors of age, manufacturer, location, and size. Since the results of this project will be used as input regarding age-based replacement requirements, representation of the collected PRV population by age was the most important criteria. Representation for factors of manufacturer, location, and size were intended to be inclusive of the range, but not necessarily as strictly proportional to the collected PRV population.

The PRV test matrix breakdown by age is shown in Figure 17. The reported PRV service age is determined by the difference between the year removed from service and the stamped date of manufacture on the PRV. For PRVs collected in 2008 and 2009 by Battelle the storage time between 2008 and 2011 is not included in the calculation of service age.

The PRV test matrix breakdown by manufacturer, location, and size is shown in Figure 18, Figure 19, and Figure 20 respectively. Note that any PRVs which had unidentified information (manufacturer or unspecified location) were not included in the test matrix.

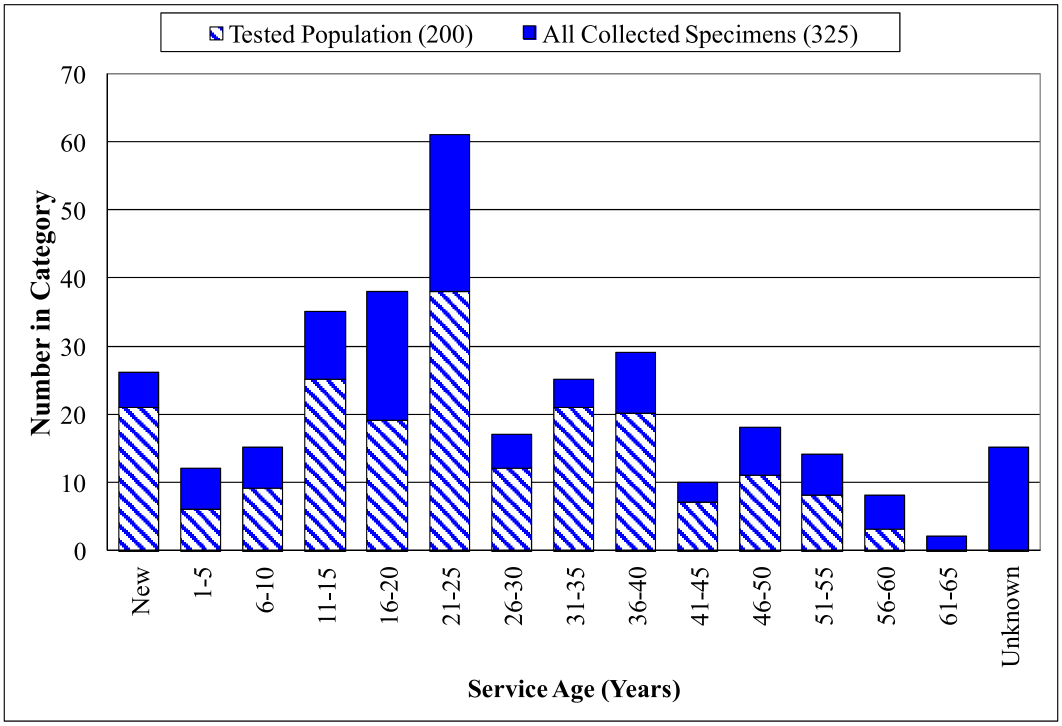

Figure 17. PRV Test Matrix Breakdown by Age

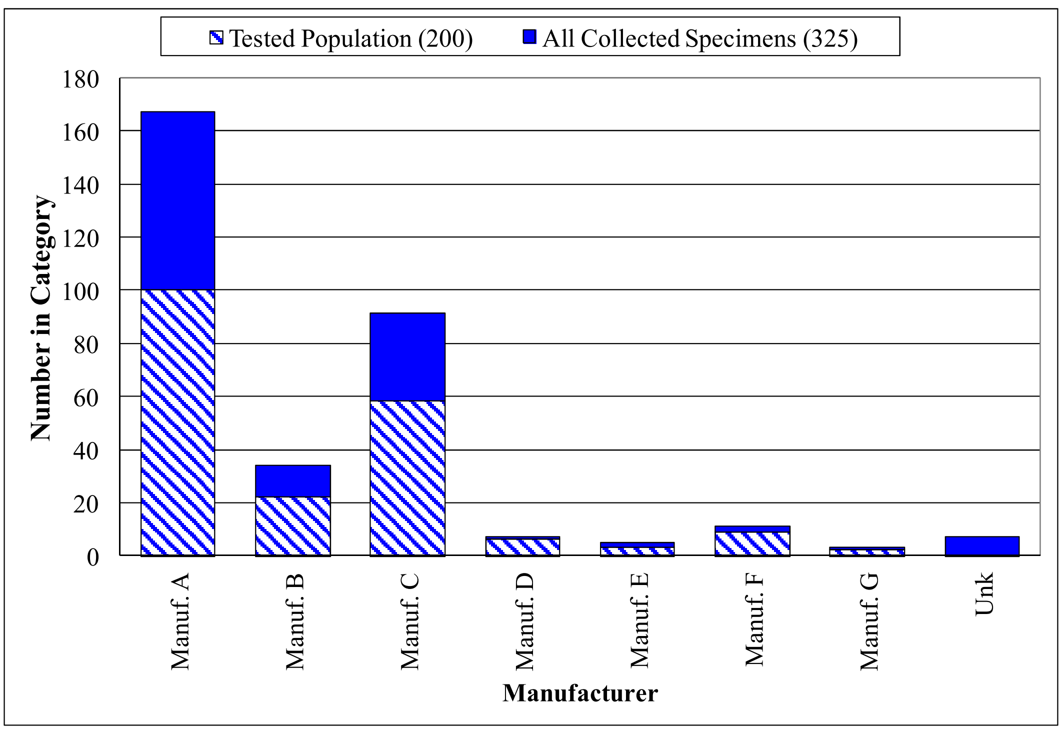

Figure 18. PRV Test Matrix Breakdown by Manufacturer

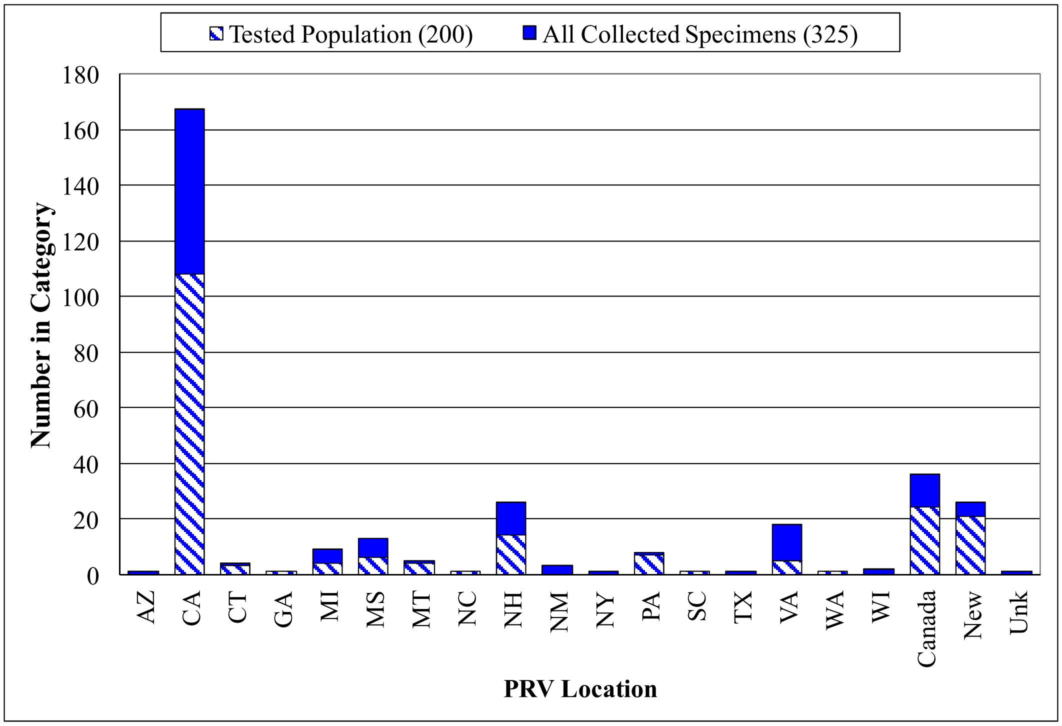

Figure 19. PRV Test Matrix Breakdown by Location

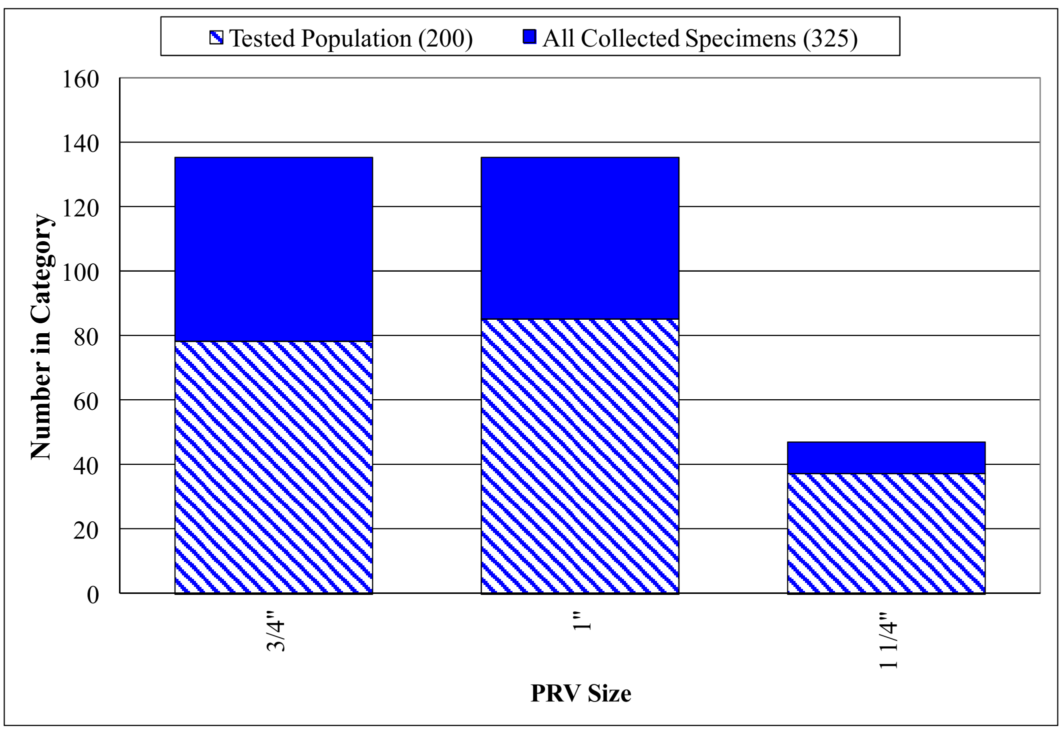

Figure 20. PRV Test Matrix Breakdown by Connection Size

2.4 PRV Set Pressure Tolerances

As this study was being conducted, Battelle became aware that over a period of time PRV manufacturers set 250-psig set pressure PRVs at a slightly higher tolerance to meet both UL 132 and ASME Section VIII requirements. This was due to a California Title 8 requirement that only ASME rated PRVs could be used on ASME containers. Since California's adoption of the 1998 version of NPFA 58, UL PRVs can now be used without a California setting.

For domestic ASME tanks, per NFPA 58, PRVs have both ASME/National Board and UL regulatory approvals. ASME section VIII, division 1 requires a STD of +10% / -0% of the marked set pressure (for a marked 250-psig PRV the range is then 250 to 275 psig). The UL approval is to UL 132 in which set and final STD are based on a combination of the 250-psig to 275-psig range and the actual average STD data from the initial samples submitted for UL approval. Due to the UL requirements the actual STD specifications can be different from one PRV model to another but are within the 250 to 275 psig ASME requirement.

To meet the California requirement several manufacturers would set the STD range at the high end of the ASME specification. For identification these PRVs have unique part numbers and/or include the marking "California Setting 275 psig". As shown in Figure 21, RegO provided an example of the differences between the PRVs made for use in California and elsewhere in the USA.

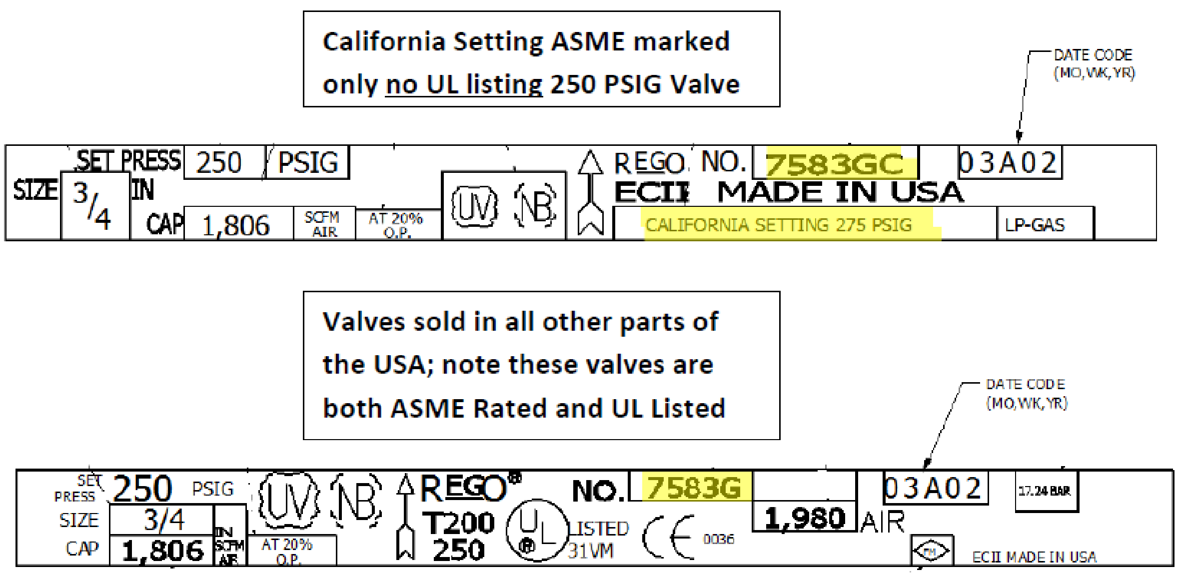

Figure 21. Example of PRV Markings for ASME marked RegO PRVs for use in California and ASME rated and UL listed RegO PRVs for use in Other Parts of the USA

In the results section, PRVs that were sold for use in California prior to their adoption of NFPA 58 are marked separately to show that these PRVs likely were set to a higher STD range when manufactured (see Figure 32). These higher initial set pressure tolerances are likely contributing to the statistically significant higher STD pressures for older PRVs as presented in Section 4.0.

3.0 Performance Testing of Propane Pressure Relief Valves

3.1 Overview

The test protocol (see Figure 8) for this project was provided in Section 1.0. The overall intent of the test protocol is to simulate the real world conditions in which a PRV would be required to function. The most frequent real world event of this type is expected to be the relief of excess pressure due to high ambient temperatures coupled with an overfilled tank. This event is characterized by a very gradual pressure rise rate and elevated temperature of the PRV.

The simulation of a fire event was not included in the modified protocol. While it is desirable for a PRV to actuate in the event of fire exposure, the high variability of fire impact on the propane tank and PRV makes it difficult to characterize a general response that should be simulated in a test protocol.

Appendix B includes detailed documentation of the protocol development. The test protocol includes considerations for conditioning and the STD test. Specifically, these include:

- Condition the PRV in a propane environment prior to testing
- Heat the PRV to 130°F during the STD test
- Increase the pressure on the PRV from 65 percent of nominal set pressure[5] at a rate of 0.24 psi/min

The STD test is completed when specified flow criteria are met or when the applied pressure reaches 375 psig.

3.2 PRV Conditioning

There are two objectives to the conditioning of the PRV in a propane environment prior to test. The first is to decrease the effect of the PRV not being subjected to any pressure for a substantial period of time prior to testing. Compared to a new PRV tested to UL 132 protocol within days to weeks of manufacture, the field collected PRVs may have been sitting on a shelf, in a laboratory controlled environment, with no applied pressure for several months between removal from the field and performance testing. The second objective in conditioning is to counteract hardening of the propane gasket that may occur as it is exposed to an oxygen-containing environment while it is out of service and awaiting testing. A PRV was conditioned in a propane environment for at least 7 days prior to testing using field-available propane obtained from a local propane marketer. The PRVs were conditioned at a pressure of about 60 to 100 psig. Ambient temperature variation leads to small fluctuations in PRV conditioning pressure. Additionally small leaks in the conditioning rig (most notably where the PRV is installed) resulted in the pressure bleeding down slightly each day. Any PRVs that had a noticeable drop in conditioning pressure were recharged each day that new PRVs were installed on the conditioning rig.

Figure 22 contains a picture of the conditioning rig. The conditioning rig allows for up to 15 PRVs to be conditioned at any time, enabling 3 PRVs to be tested each weekday. Each conditioning pipe has an isolation valve to allow for independent installation and removal of

[5]For testing simplicity and quality control, all PRVs were subjected to an initial pressure of 162.5 psig (65 percent of 250 psig)

PRVs. The isolation valves are connected to a common manifold. The manifold is connected on one end to a vacuum pump (to remove air from the conditioning pipe prior to fill) and on the other end to a 20-lb propane cylinder that provides the propane fill.

After filling and isolating the PRV conditioning pipe, liquid leak detector was used to identify and correct any leaks in the conditioning pipe. The stable pressure in the pipe was marked using a piece of tape on the pressure gage to provide a reference on the amount of leakage between daily checks.

Figure 22. PRV Conditioning Stand

3.3 Start-to-Discharge Testing

Following conditioning, the PRVs were subjected to a start-to-discharge (STD) test. Figure 23 shows the STD test stand. The STD test stand includes provisions for heating the PRV and for a slow pressure rise. A schematic of the test equipment is shown in Figure 24.

Breathing air from a bank of 12 to 15 gas cylinders is regulated to supply approximately 400 psig air to a 30-gallon ASME vessel. The vessel supplies air to three isolated PRV test branches. The three branches enable three PRVs to be tested simultaneously. A pressure transmitter monitors the pressure applied to the PRV. The pressure is used in a closed feedback loop with the automatic pressure regulator[6] to maintain the desired PRV pressure. A high pressure flow meter

[6] Note that while the automatic pressure regulator on PRV 1 path requires a dome loading, the automatic pressure regulators on PRV paths 2 and 3 do not have this requirement due to different models being implemented. All of the automatic pressure regulators had similar and acceptable ability to control the PRV pressure as required by the test protocol.

is used to monitor flow, the measured criterion that indicates a PRV has opened. The PRV is heated using a 60W flexible silicone heater controlled by a PID controller. The controller has a setpoint of 130°F and is autotuned for good thermal response. A thermocouple is sandwiched between the PRV body and the heater. The same thermocouple provides feedback to both the PID controller and the data logging system. The PRV is loosely wrapped with insulation to give a more stable temperature control.

In the picture shown as Figure 23 only one PRV is installed. The PRVs are installed in the large diameter pipes at the right end of the image. The installed PRV is already wrapped in insulation that helps improve the elevated temperature stability of the PRV.

Figure 23. Start-to-Discharge Test Stand

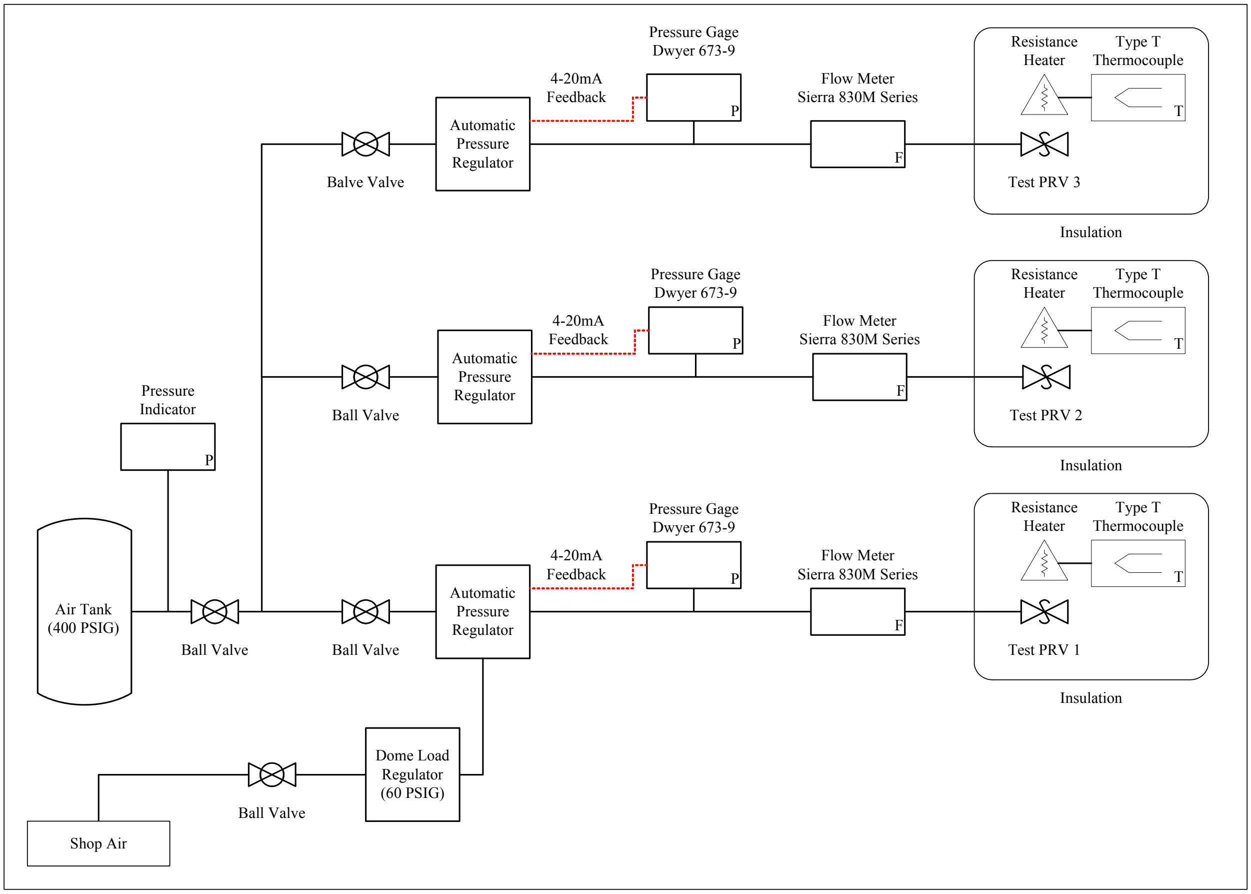

Figure 24. Start-to-Discharge Test Stand Schematic

The pressure transmitters, flow meters, and thermocouples are connected to Data Acquisition (DAQ) hardware on a Windows PC running National Instruments' LabVIEW. The DAQ hardware also provides the command signals to the automatic pressure regulators. The user interface, shown in Figure 25, allows for user inputs to characterize and control the test and provides visual indication of measured data. All test data are logged to a data file once each second.

The LabView control program enables two modes of operation. The first is a leak check mode. After a PRV is installed on the STD rig but before it is heated or wrapped with insulation, it is leak tested by applying 50 to 100 psig and using a liquid leak detector fluid. The second mode of operation is the STD test protocol. The control program monitors and records all sensors and initiates appropriate control action based on the data.

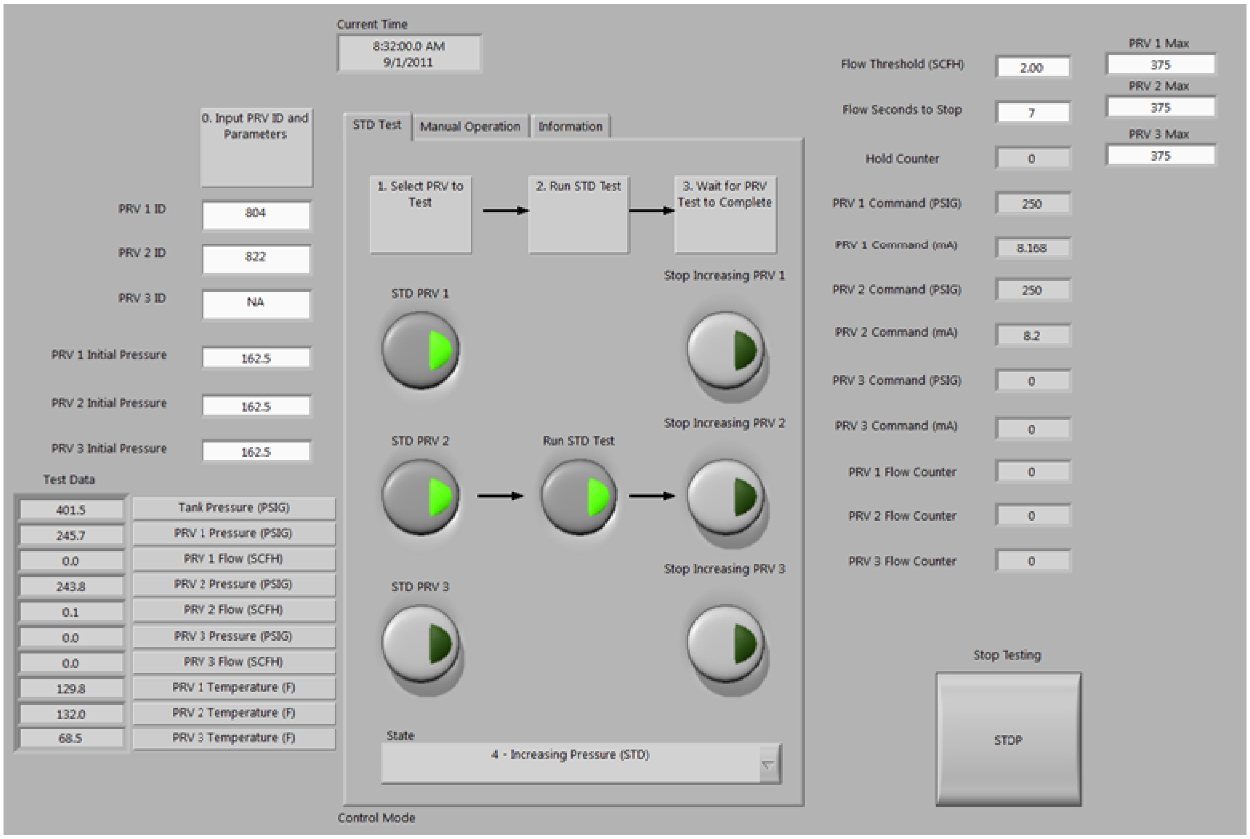

Figure 25. LabView Control Screen

Examples of the thermal response of the PRV are shown in Figure 26 and Figure 27. The PRV rapidly approaches setpoint temperature, reaching 120°F within minutes of starting the test. Since the heater wattage and PID parameters are fixed for all tests, the time to reach steady state is dependent upon the thermal mass of the PRV. When the temperature data is examined in more detail, a steady state response of 130°F +/- 3°F is observed. Note that this measurement is directly adjacent to the heating element so the temperature fluctuations are at a maximum. As the heat is conducted into the PRV, the temperature of internal components would be expected to vary even less than at the measurement point.

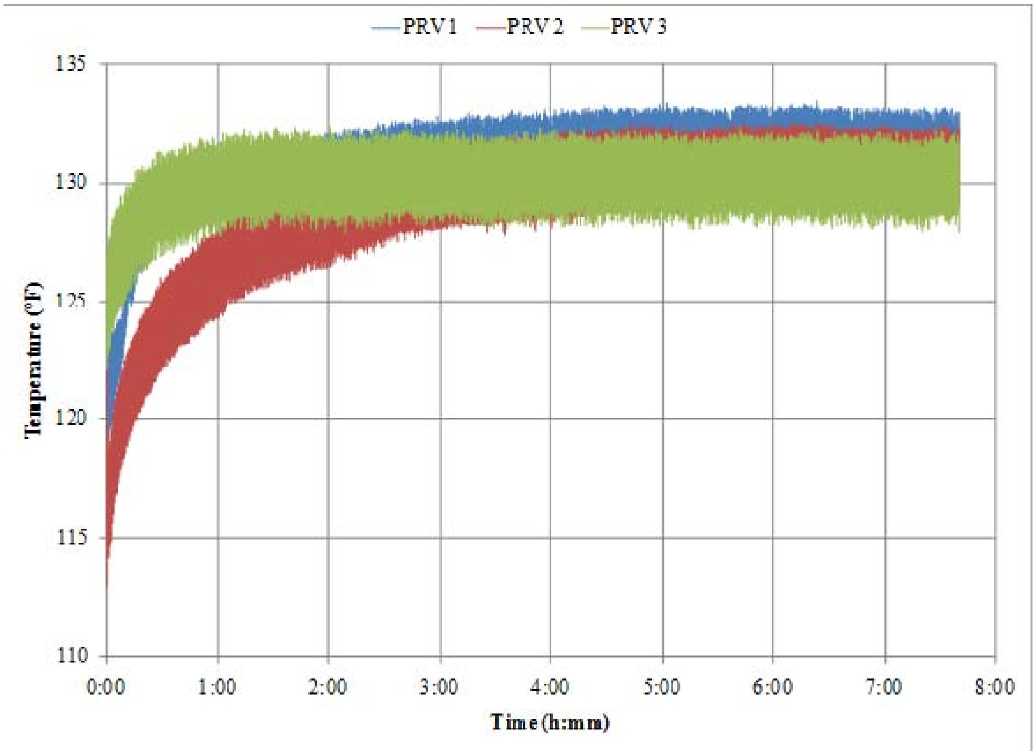

Figure 26. Thermal Response of PRVs over Entire STD Test

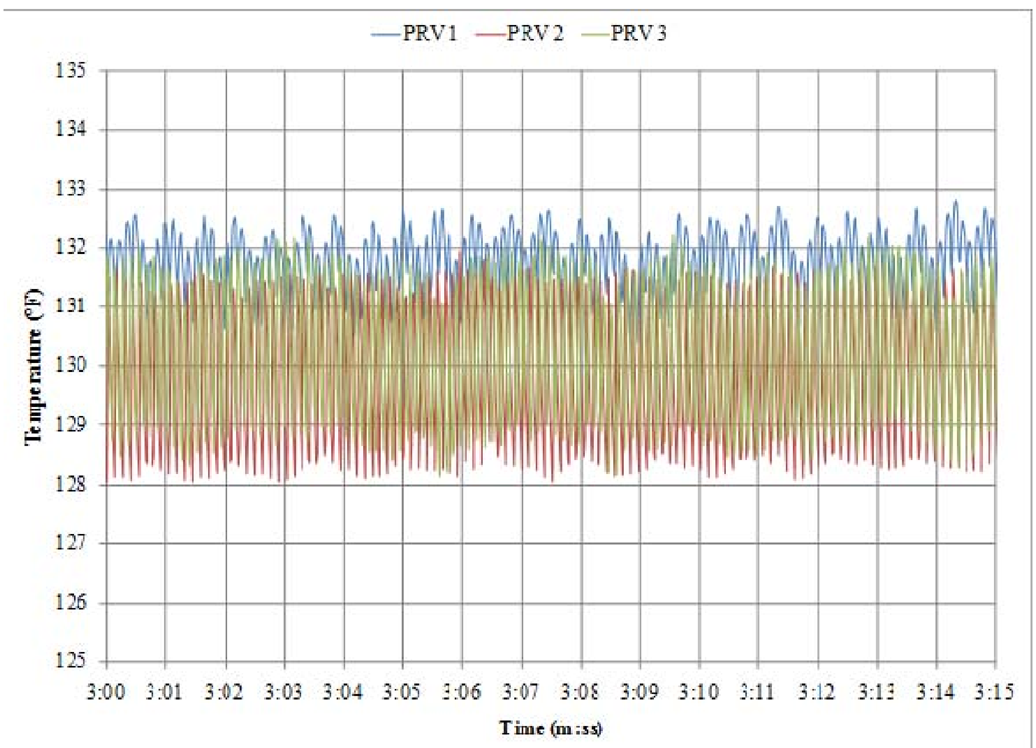

Figure 27. Thermal Response of PRVs (Zoom)

Figure 28 and Figure 29 show pressure and flow data for a single PRV during a typical STD test. Battelle made the following observations:

1. For all tests, the initial pressure command is 162.5 psig (65 percent of 250 psig). The same initial pressure is used for all tests regardless of marked PRV pressure as a conservative fail-safe approach. The initial pressure on the PRV shown in Figure 28 is approximately 155 psig. This is due to an offset in the control system. The offset is of minimal impact since actual PRV pressure is measured and recorded for determining the STD pressure.
2. The pressure measurement shows a small degree of variation, about 5 psig (1percent of the sensor range).
3. Periodic flow measurements above 1 SCFH are recorded throughout the test. The automatic pressure regulators adjust the PRV pressure to the command setpoint. Over time a small error accumulates and eventually a slightly larger adjustment is made by the regulator resulting in a flow measurement above zero. The STD criteria require several successive flow measurements over zero to increase confidence the PRV has opened.

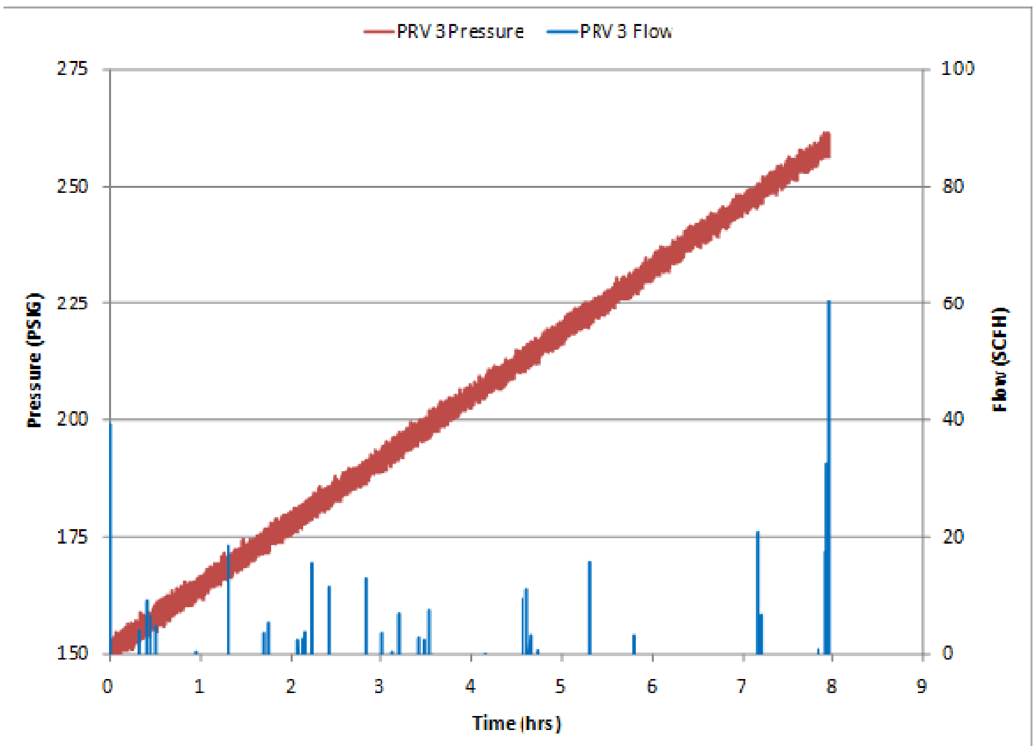

Figure 28. Sample STD Test Pressure and Flow Data

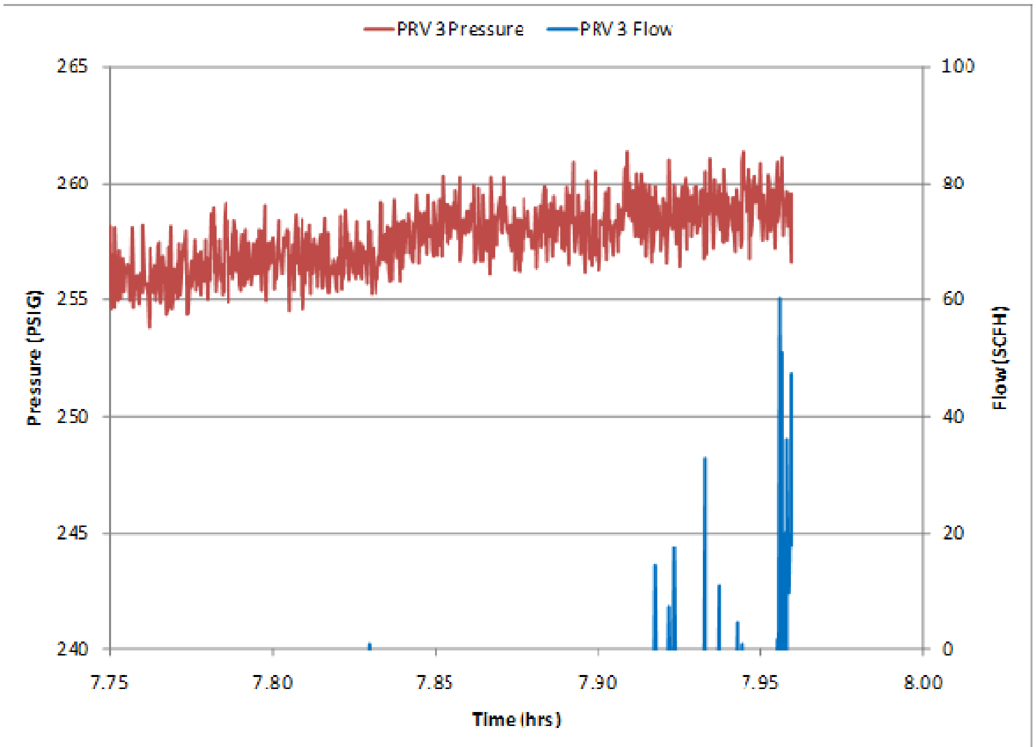

Figure 29. Sample STD Test Pressure and Flow Data (Zoom)

4.0 Test Results and Statistical Analysis

4.1 Performance Criteria

Because there is no performance standard for PRVs used in the field, the UL 132 STD criteria for **new** PRVs was used as an indicator of PRV performance. This does not infer that if a field-removed PRV performs outside the criteria for new PRVs it is not protecting the tank; rather it is an indicator of its performance against expectations for newly manufactured PRVs. For the remainder of the report the acronym NPC for "New Performance Criteria" is used when comparing the test results against the UL 132 STD criteria for newly manufactured PRVs.

The primary performance criteria used in the test program include:

- PRV did not relieve by 375 psi (1.5x the working pressure of a propane tank, equivalent to the hydrotest pressure)
- PRV STD pressure below the set pressure
- PRV STD pressure higher than 120 percent of the set pressure (represents when the PRV should be fully open)

The maximum test pressure was limited to 375 psig to maintain safe operation of the test rig by the operator performing the tests. The test program was designed to stress the PRV without creating a situation that may have been dangerous for those conducting the test. A secondary reason for limiting the maximum test pressure to 375 psig is that this represents the hydrotest pressure for ASME tanks with a working pressure of 250-psig.

The criteria specifying a STD 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 STD pressure lower than the set pressure criteria was chosen because it represents a potential chronic leak issue for a PRV, particularly if the PRV fails to reseat.

Note that these two performance criteria have different consequences. A PRV that leaks or opens before STD will protect the tank from high pressures. Additionally, low STD pressures that result in leaks or frequent discharges are more likely to be identified by the propane marketer or consumer due to the odorant used in propane. A STD pressure in excess of 120 percent of the set pressure is considered high for new PRVs, but still below the hydrostatic test pressure of a tank designed for 250 psig working pressure.

4.2 Overall Test Data Summary

Figure 30 (250 psig) and Figure 31 (275 psig) compare the STD pressure against the NPC and age for the 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 set pressure, STD pressure, and full open pressure limits as specified in UL 132. The three different data symbols represent the pre-test visual inspection results (● = good; ▲ = marginal; **X** = poor). The darker gray band represents the range of acceptable PRV performance against the NPC. Data points with the label 'DNO' signify PRVs that did not open by 375 psi (1.5x the working pressure of a propane tank, equivalent to the hydrotest pressure). Significant differences between ages are evident by the variation in the vertical spread of the data points.

PRVs receiving marginal and poor visual inspection ratings tend to increase with PRV age (see Figure 12). This trend is also seen in Figure 30 and Figure 31 with a high number of good inspection ratings for younger PRVs.

There are few obvious trends in the data. For 250-psig PRVS, STD pressures range from 50 psig below set pressure to 100 psig above set pressure. The total band of pressure ranges is smaller for newer PRVs (<5 years). The band of STD pressure ranges does not appear to gradually widen with age; rather it expands somewhere around 10 to 15 years and remains approximately the same span for all future years. PRVs with good, marginal, and poor ratings are scattered throughout with a majority of PRVs receiving a 'marginal' or 'poor' rating occurring outside the bounds of the NPC.

For 275-psig PRVs, STD pressures range from 80 psig below set pressure to 70 psig above the set pressure (ignoring the 2 PRVs that did not open). For these PRVs, the range of STD pressures as a function of age appears to be small at lower ages (15-20 years) and gradually expands as the PRV age increases.

Figure 30 data are repeated in Figure 32 with 250-psig PRVs that were likely set higher for installation in California differentiated. Several of the California setting PRVs shows higher STD pressures. Nineteen of the twenty-eight California setting PRVs had STD pressures over

275 psig (110 percent of 250 psig). Only 9 California setting PRVs had STD pressures over 312.5 psig (110 percent of 275 psig). The remaining California setting PRVs (9 of the 28) had STD pressures between 230 and 275 psig.

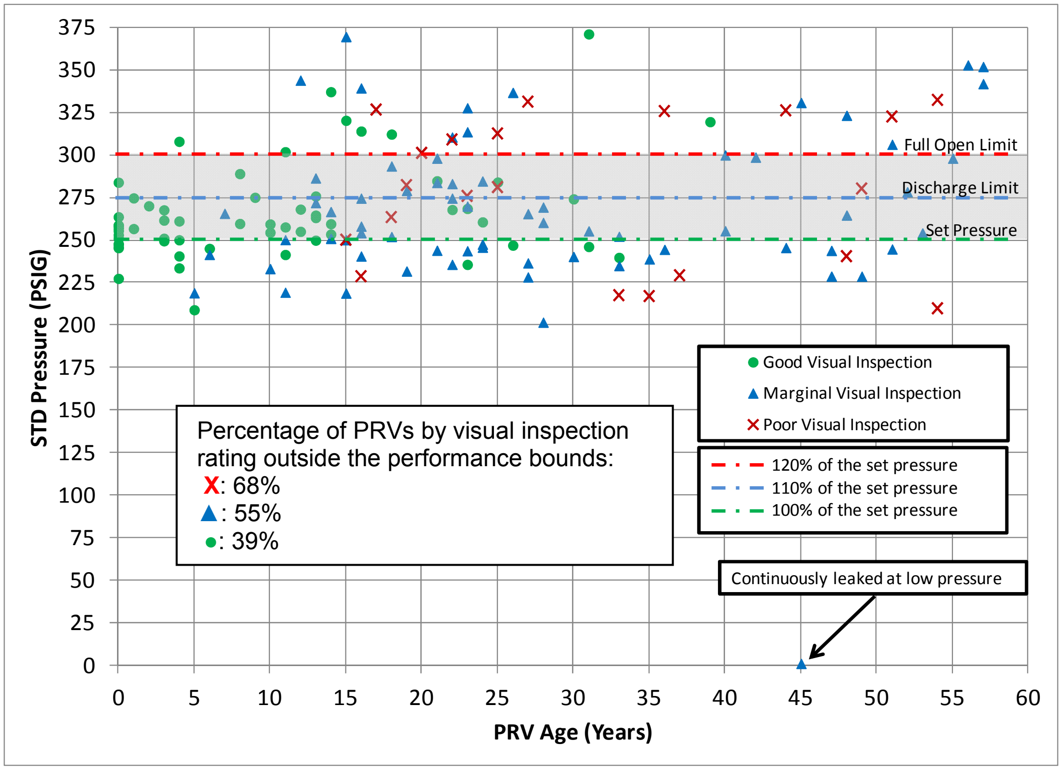

Figure 30. Test Results with Visual Inspection Ratings, 250-psig Set Pressure PRVs

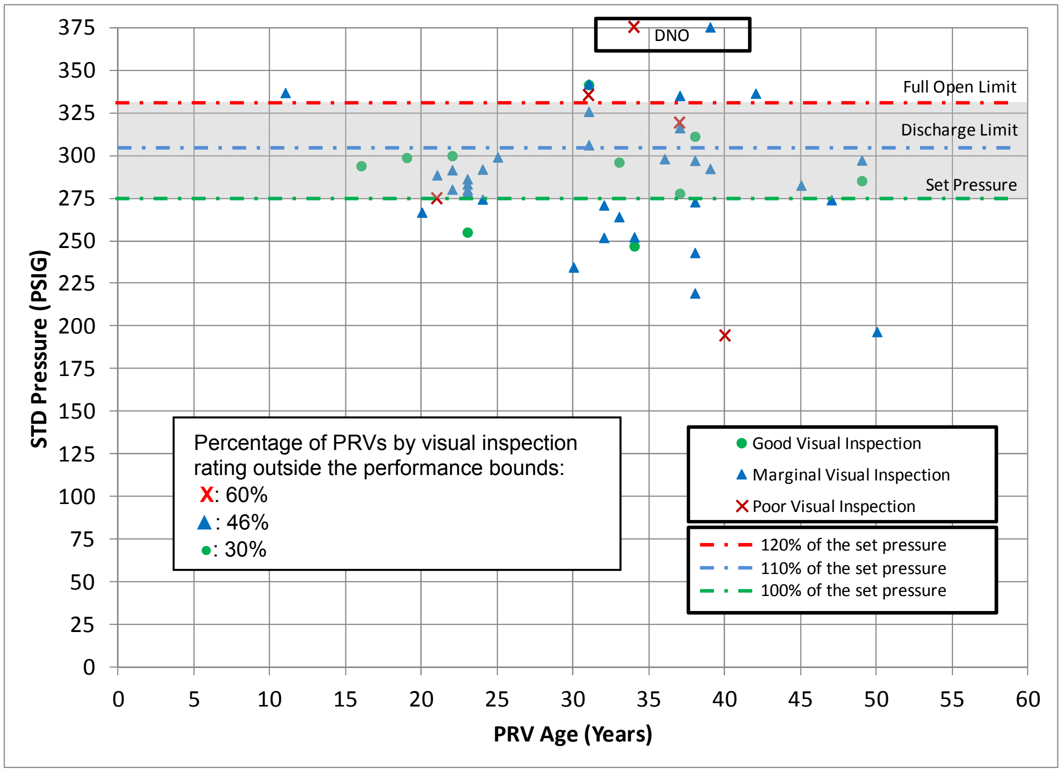

Figure 31. Test Results with Visual Inspection Ratings, 275-psig Set Pressure PRVs

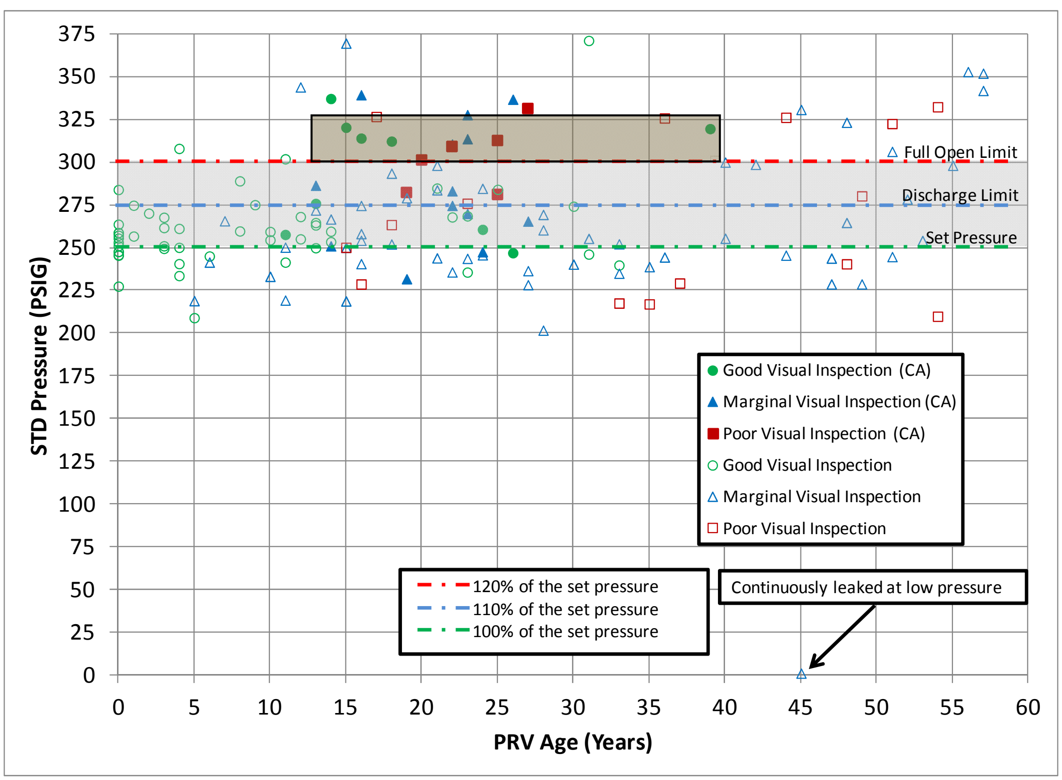

Figure 32. Test Results with Visual Inspection Rating, 250-psig Set Pressure PRVs.
PRVs Set Higher for Installation in California Highlighted

In Figure 33 the breakdown of PRVs that performed outside the bounds of the NPC (STD below set pressure or greater than 120 percent of set pressure) is given. In general, the ¾" size PRVs had the highest compliance with the NPC; about 65 percent to 70 percent met the criteria. No group stands out as particularly poor with respect to PRV size; 40 percent to 60 percent meeting the NPC is typical.

PRV behavior outside the bounds of the NPC is further broken down for assorted sizes in Figure 34. In general, ¾" PRVs tended to have the lowest percentage that had STD pressures above 120 percent of set pressure. Both PRVs that did not open were 1" 275-psig PRVs.

Similar overall breakdowns are presented for groups by manufacturer (Figure 35) and age (Figure 37). Detailed breakdowns of the performance outside the bounds of the NPC are also given for groups by manufacturer (Figure 36) and age (Figure 38).

As demonstrated in Figure 32, some PRVs were likely installed with a higher initial set pressure to meet STD requirements specified in both ASME Section VIII and UL 132 (PRVs within dark colored square). Therefore, some PRVs classified as not meeting the NPC for 250-psig set pressure PRVs in the following figures may actually fall within the NPC bounds based on actual set pressure if for example the PRVs were initially set to 270 psig.

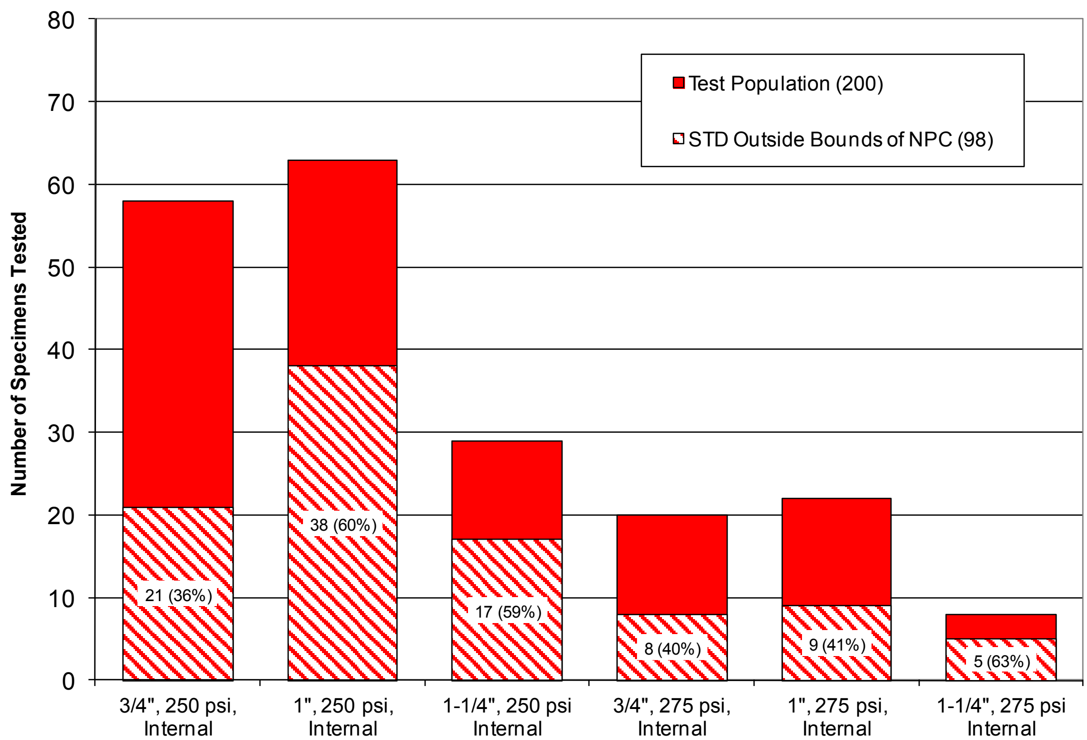

Figure 33. Breakdown of PRVs with STD Outside the Bounds of the NPC by Size

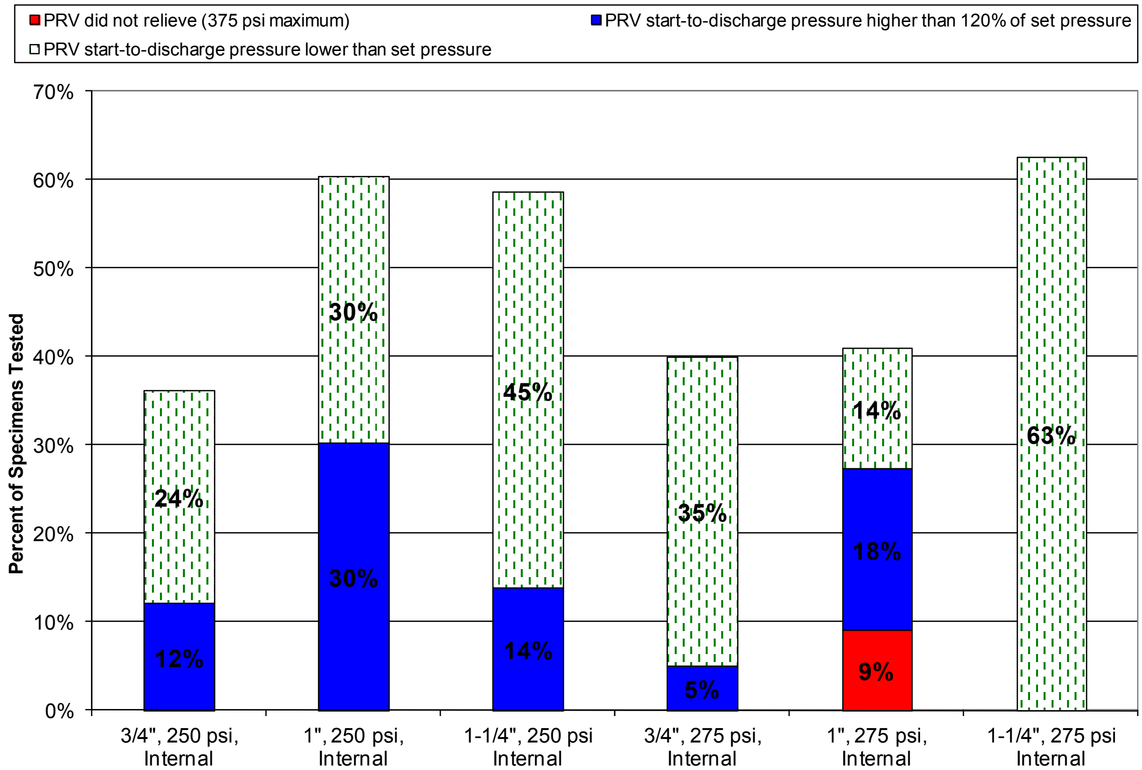

Figure 34. Detailed Breakdown of PRVs with STD Outside the Bounds of the NPC by Size

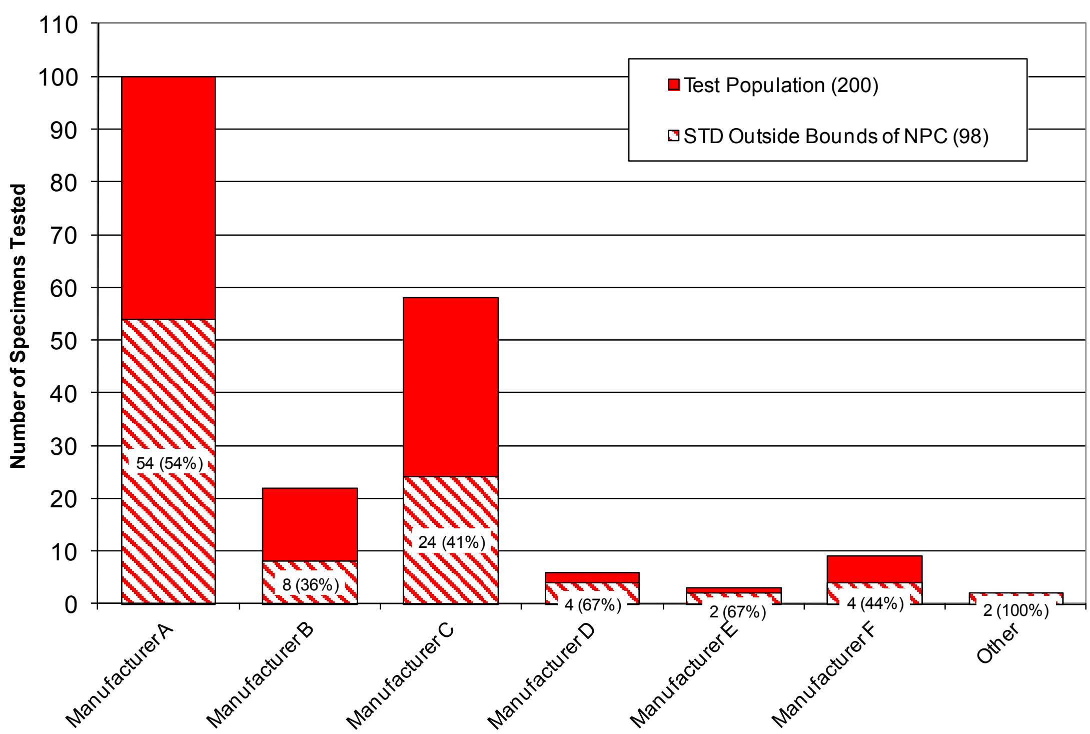

Figure 35. Breakdown of PRVs with STD Outside the Bounds of the NPC by Manufacturer

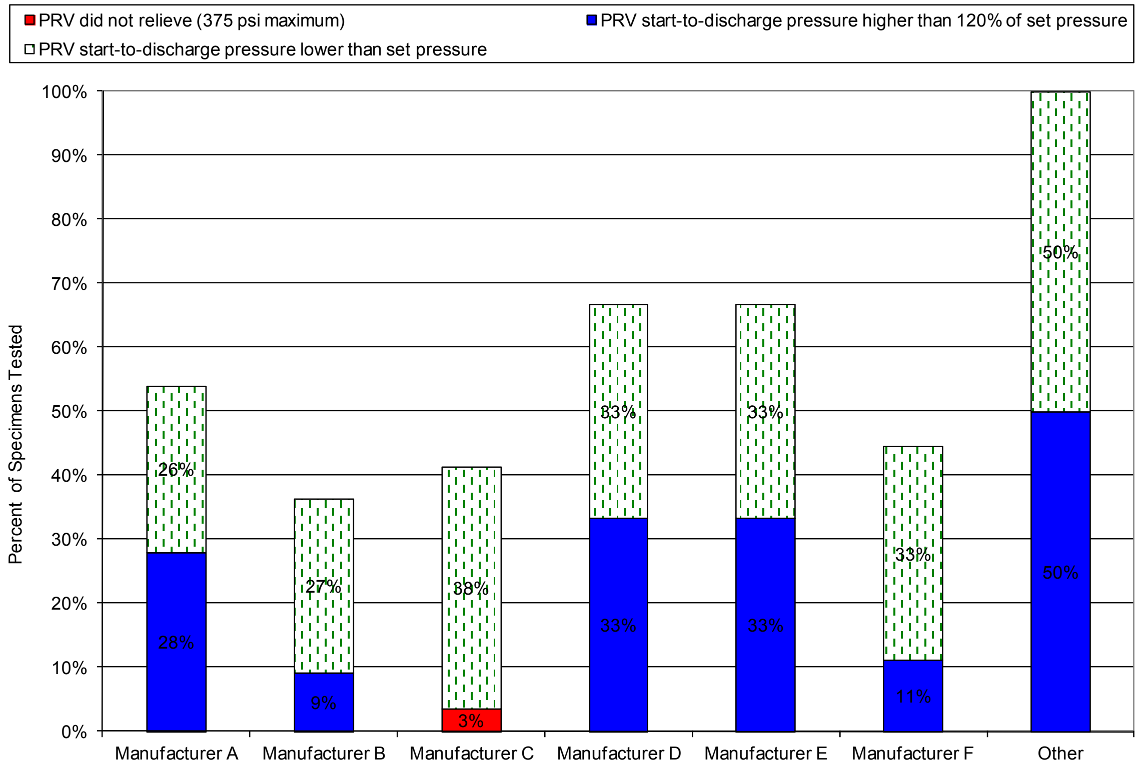

Figure 36. Detailed Breakdown of PRVs with STD Outside the Bounds of the NPC by Manufacturer

Breakdowns by manufacturer of PRVs with STD pressures outside the bounds of the NPC are shown in Figure 35 and Figure 36. For manufacturers with a significant quantity of PRVs tested, anywhere from 36 percent to 54 percent of PRVs did not meet the NPC. Manufacturer A had the highest percentage of PRVs falling outside the bounds of the NPC. The split was approximately equal between PRVs that discharged too early and too late. Similar splits were observed for Manufacturers D, E, and Other, although with far fewer PRVs tested. The majority of performance issues for Manufacturers B and C were early STD pressures. Manufacturer C had no PRVs discharge higher than 120 percent of the set pressure, but did have both PRVs that did not open by 375-psig. Since no other STD pressures greater than 120 percent were observed for this manufacturer, it would suggest that factory setting of the PRV at a high pressure is likely not the cause of the two PRVs not opening by 375-psig. Forensic analyses indicated that the reason for the observed behavior was most likely due to the PRV stems becoming ‘stuck’ to the brass spacer guides during service.

Figure 37 and Figure 38 show the age breakdown of PRVs that did not meet the NPC. For PRVs 25 years age and younger, approximately 30 percent to 50 percent of the test population fell outside the bounds of the NPC. Almost all of the performance issues were low STD pressures for PRVs under 10 years in age. Although high STD pressures begin to appear after 10 years, there doesn’t appear to be a discernible trend of their percentage increasing with age. Note that the two PRVs that did not open by 375-psig were over 30 years age.

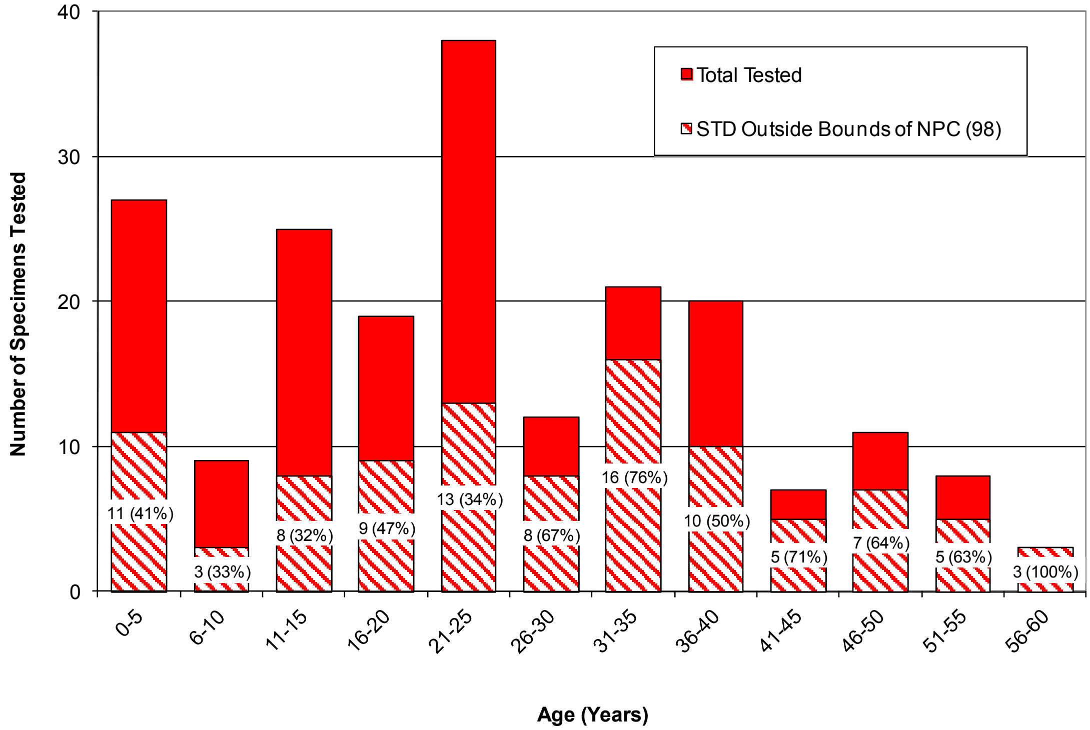

Figure 37. Breakdown of PRVs with STD Outside the Bounds of the NPC by Age

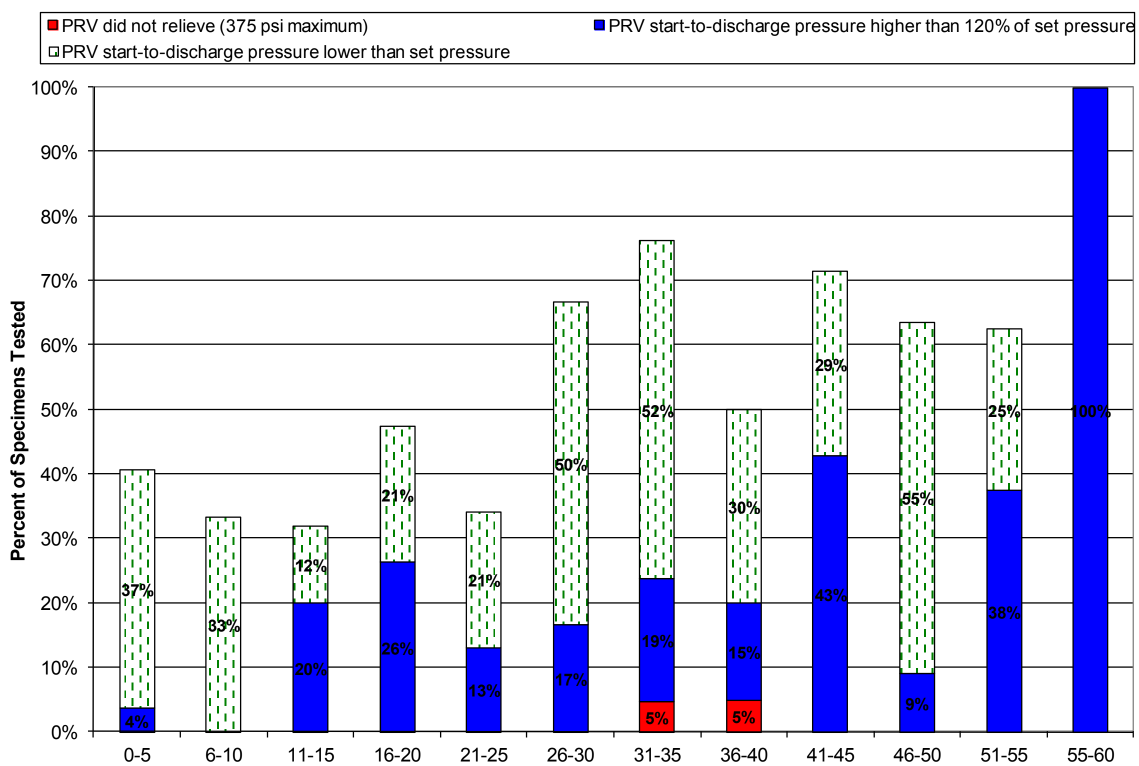

Figure 38. Detailed Breakdown of PRVs with STD Outside the Bounds of the NPC by Age

4.3 Test Data Discussion

Results for 199 PRVs are presented in the previous figures. PRV #746 was found to have significant physical damage. The PRV leaked significantly and continuously when installed on the conditioning rig such that a conditioning pressure could not be maintained for any length of time. Since the damage was likely due to handling after field service, the PRV was not included in the STD test results. PRV #746 is shown in Figure 39.

Figure 39. Top View of PRV 746 Showing Significant Physical Damage

There are several other high level observations that can be made from Figure 30 and Figure 31 (scatter plots that compare the STD pressure for 250-psig and 275-psig set pressure PRVs against the NPC and age for the PRVs tested in this program). Details on these and other PRVs are discussed in more detail in Section 5.0 on Forensic Analysis:

- Did not open at 375 psig
  - PRV 122 – 1” Internal, 275-psig Set Pressure, 34 Years
  - PRV 760 – 1” Internal, 275-psig Set Pressure, 39 Years
  - Both PRV 122 and PRV 760 are identical models from the same manufacturer. PRV 728 is also an identical model that is a 1” Internal, 275-psig set pressure PRV that was tested and opened at 292 psig.
- Leaked continuously at low pressure (1 psig)
  - PRV 187 – ¾” Internal, 250-psig Set Pressure, 45 Years, Leaked continuously at 25 psig
- Opened at very low pressure
  - PRV 547 – 1¼” Internal, 275-psig Set Pressure, 37 Years, Opened at 219 psig
  - PRV 597 – 3/4” Internal, 275-psig Set Pressure, 45 Years, Opened at 194 psig
  - PRV 733 – ¾” Internal, 275-psig Set Pressure, 50 Years, Opened at 196 psig

4.4 Statistical Analysis of Results

Box plots were constructed to determine if there are differences between PRV performance against the NPC based on environmental conditions (Figure 40), manufacturer (Figure 41), and PRV size (Figure 42). The boxes represent where 50 percent of the data for each category fall.

The line in the center of the box is the median value and the '+' symbol is the mean value for the data in a particular category. The lines extending from the box represent the maximum and minimum range of the data while the individual dots plotted are the outliers. If there are significant differences between the variables there would be noticeable variation of the vertical spread or a distinct shift of the data points taken as a group.

Non-parametric one-way ANOVAs were performed using the software program SAS® to determine if there were any statistically significant differences between boxes in each plot. The following statistically different observations were made:

1. For 275-psig PRVs, Manufacturer C had statistically significantly lower PRV STD pressure results than Manufacturers A and B
2. For 250-psig PRVs, 1¼" PRVs had statistically significant lower PRV STD pressures than ¾" or 1" PRVs
3. For 275-psig PRVs, ¾" PRVs had statistically significant lower PRV STD when compared to 1" PRVs. (1¼" PRVs are not statistically different from either 1" or ¾")

It is difficult to conclusively identify a root cause for these statistical differences; however a few observations can be made.

Observation 1 – Manufacturer C had statistically significantly lower PRV STD pressure results than Manufacturers A and B for 275-psig PRVs

- Battelle has observed age-related performance correlations for PRVs. For 275-psig PRVs the observed difference could be due to relative age differences among the three manufacturer groups. That was investigated, but the distributions of PRVs by age for each of those three manufacturer groups were similar.
- Manufacturer C did have the lowest percentage of poor visual inspection results (Figure 13). Although the visual inspection ratings are subjective, the intent was to characterize the general condition and operability of the PRV.
- The difference could be due to a specific design characteristic of Manufacturer C that the modified test protocol has a higher effect upon.
- For Manufacturer C almost all of the STD performance issues were low STD pressures (Figure 36). Although that plot includes both 250- and 275-psig PRVs, the lack of any high STD numbers gives credibility to this statistical observation.

Observation 2 – 1¼" PRVs had statistically significant lower PRV STD pressures than ¾" or 1" PRVs for 250-psig PRVs

- The average value for 1¼" PRVs was very close to 250-psig, indicating a substantial portion of the population had lower STD values (Figure 42). This could be attributed to the installation on the STD test equipment. Contact area increases with thread size and it is more difficult to obtain a good seal on larger pipe threads. Coupled with the repetitive use of fittings on the test stand, this could be a source for the variation.

Observation 3 – ¾" PRVs had statistically significant lower PRV STD when compared to 1" PRVs (1¼" PRVs are not statistically different from either 1" or ¾") for 250-psig PRVs

- The average STD pressure for the ¾", 275-psig PRVs was around 271 psig while the average STD pressure for the 1", 275-psig PRVs was around 305 psig. Both PRVs that did not open fell in the 1" category plus the 1" PRVs had an average age of 34 years. In contrast, the average age of the ¾", PRVs was 27 years which likely had an influence on the lower STD pressure of the ¾" PRVs. Other data indicates that PRV performance outside the bounds of the NPC tends to increase with the age of the PRV.

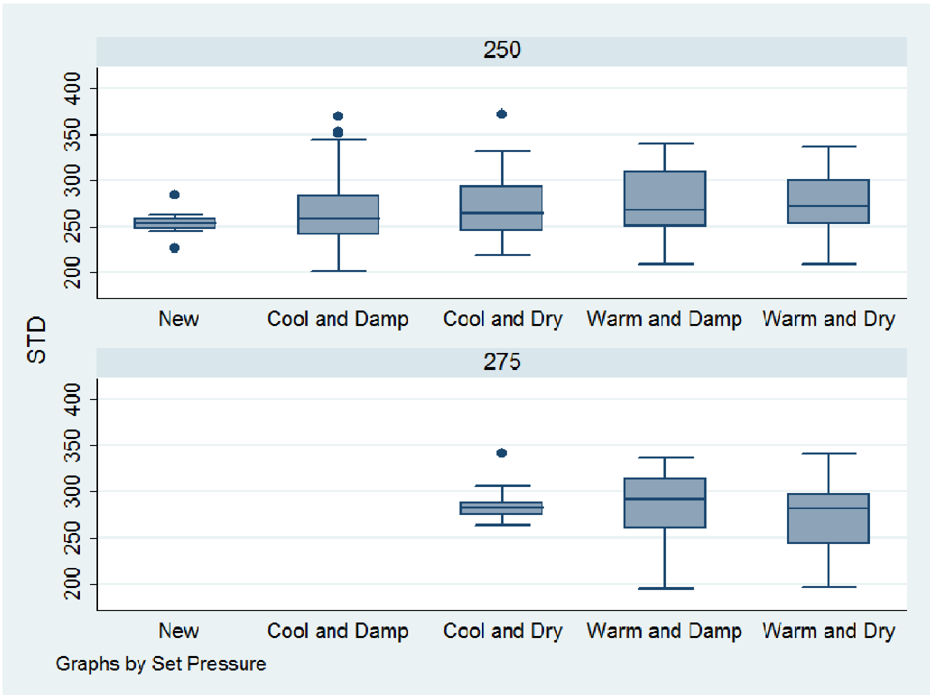

Figure 40. Box Plot of PRV STD Pressure vs. Environmental Condition

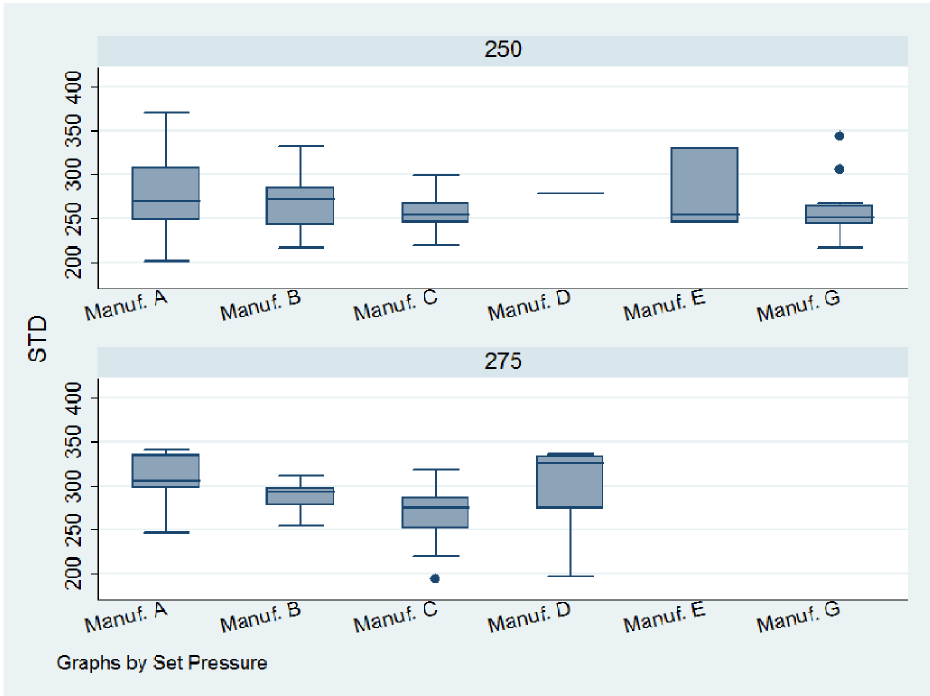

Figure 41. Box Plot of PRV STD Pressure vs. Manufacturer

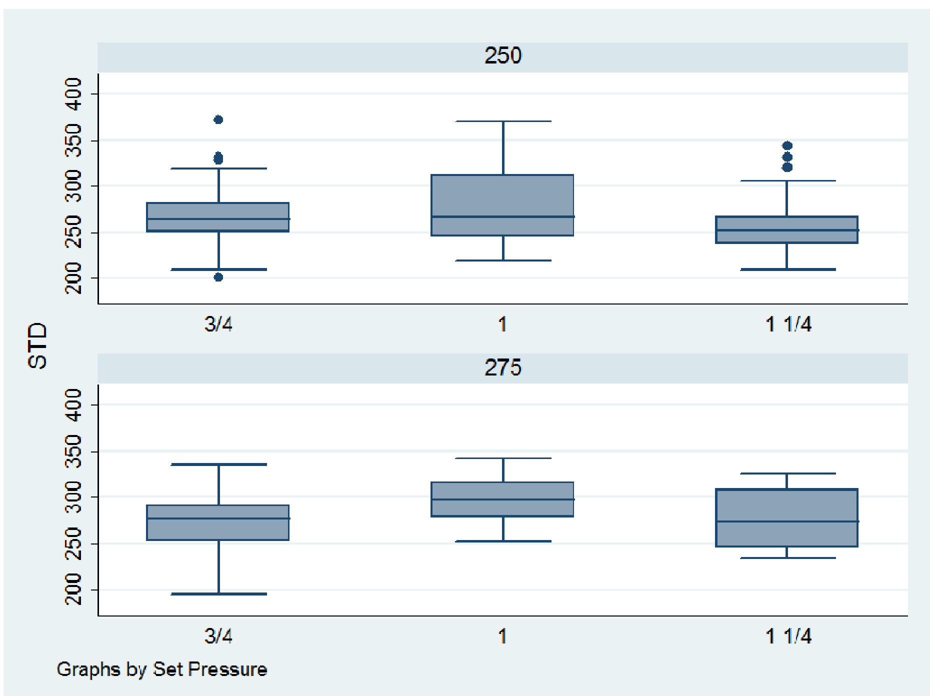

Figure 42. Box Plot of PRV STD Pressure vs. PRV Size

Logistic regression models were developed using the statistical software program SAS® to answer the following questions:

- Is there a tendency for PRVs to "stick" closed that depends on the age of the PRV?

- Is there a tendency for a PRV to open too soon (STD below the set pressure) that depends on the age of the PRV?
- Is there a tendency for a PRV to open too late (STD >110 percent or >120 percent of the set pressure) that depends on the age of the PRV?

In statistics, logistic regression is used for prediction of the probability of occurrence of an event (sticking closed, opening too late, opening too soon, etc.) by fitting data to a logistic curve. Logistic regression allows prediction of a discrete outcome (e.g. PRV sticks closed) from a set of variables that may be continuous, discrete, dichotomous, or a mix of any of these (e.g. age). Generally, the dependent or response variable is dichotomous, such as success/failure. The linear logistic model used for this analysis has the form

$$\text{logit}(\pi) \equiv \log\left(\pi/(1-\pi)\right) = \alpha + \beta * \text{AGE}$$

where π is the probability that the indicator variable is equal to 1 (tendency to stick closed, open late, etc.), α is the intercept parameter, and β is the slope on the AGE term.

Table 1 contains p-values for parameter estimates from fitting this model for all four analyses for both 250- and 275-psig set pressure PRVs. In statistical hypothesis testing, the p-value is the probability of obtaining a result as extreme or more extreme than what was actually observed, assuming that the null hypothesis is true (there is no performance difference due to the age of the PRV). The lower the p-value, the less likely the null hypothesis will be true so the more "significant" the result. The result of a test of significance is either "statistically significant" or "not statistically significant."

Significant p-values are highlighted in Table 1. Note that the only models with significant p-values were from PRVs with set pressures of 250-psig. This is probably because of the significantly smaller sample size for the 275-psig set pressure PRVs (there are about 3 times as many 250-psig set pressure PRVs as 275-psig set pressure PRVs) as well as the larger variability in the results for 275-psig set pressure PRVs.

Table 1. p-values for Parameter Estimates from Logistic Regression of Indicator Variables on Age (years)

Analysis of Tendency To _____:	Set Pressure = 250 psi			Set Pressure = 275 psi		
	Sample size	Number Events	p-value	Sample size	Number Events	p-value
Open too Soon	153	51	0.988	45	15	0.376
Open too Late 110%	153	53	<.001[7]	45	12	0.241
Open too Late 120%	153	30	0.002[3]	45	7	0.387
Did not open	153	0	-----	45	2	0.496

For the regression models with statistically significant slopes, plots were constructed to show the probability of performance as a function of PRV age. The plots contain estimates of the probability of opening (too soon or too late) by age, indicated by solid lines. This probability is

[7] Slope p-value is significant at the .05 level of significance.

based on the experimental data. A 95 percent upper confidence bound is indicated by the dashed line. This higher probability value factors in the limited amount of PRVs tested relative to the entire population installed and the variability observed in the test data.

Figure 43 and Figure 44 show that the tendency for a 250-psig PRV (the only model with a statistically significant slope) to open 110 percent or 120 percent above the set pressure increases with age. Note that a plot is not included for 250-psig PRVs to not open since there were insufficient events (0) to populate the model.

Only two out of 200 PRVs tested (1percent of the test population) did not open after reaching 375 psig. Both of these PRVs had 275-psi set pressures and were not found to be statistically significant (could have occurred by chance) likely due to the smaller sample size for 275-psig set pressure PRVs.

As shown in Figure 43, the probability for a PRV to discharge above 110 percent of the set pressure ranged from approximately 17 to 26 percent (with 95-percent confidence) for new PRVs to 52 to 62 percent (with 95-percent confidence) for 40 year old PRVs. These results are similar to the original test program except that the probability trend for a PRV to STD above 110 percent of the set pressure is slightly steeper in this study (starts at a lower probability for newer PRVs).

PRVs that discharged late (>120 percent of the set pressure) were considered to have performance outside the bounds of the NPC. As shown in Figure 44, the probability for a PRV to discharge above this limit accelerates for PRVs older than 25 to 30 years of age as indicated by the increased slope of the line. The probability for new PRVs to open 120 percent above the set pressure can range from approximately 8 to 15 percent (with 95-percent confidence) increasing to 31 to 42 percent (with 95-percent confidence) for 40 year old PRVs. Note that these percentages refer to the response of the PRV to the applied pressure.[8]

[8] A tank pressure in excess of 300 psig (120 percent of 250-psig) is a lower probability field event that requires a combination of several external factors including a high tank fill level and unusually hot ambient weather conditions.

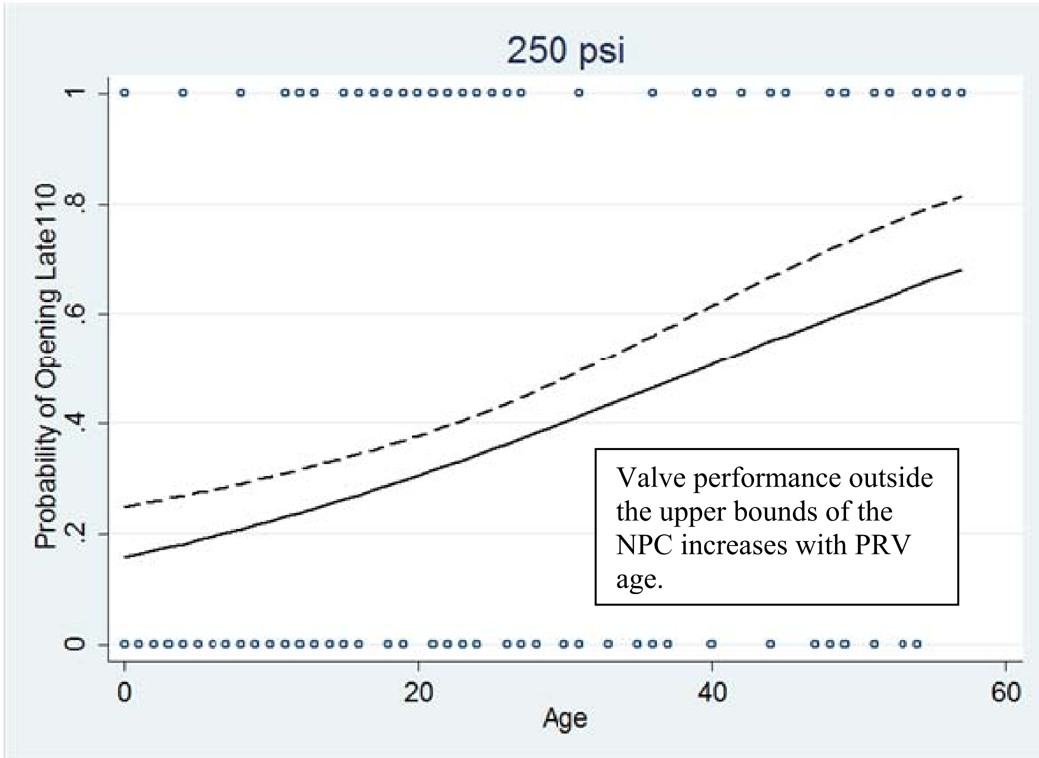

Figure 43. Estimated Probability and 95-Percent Upper Confidence Bound for Tendency to Open Late (110 percent) vs. Age (Years), 250-psig

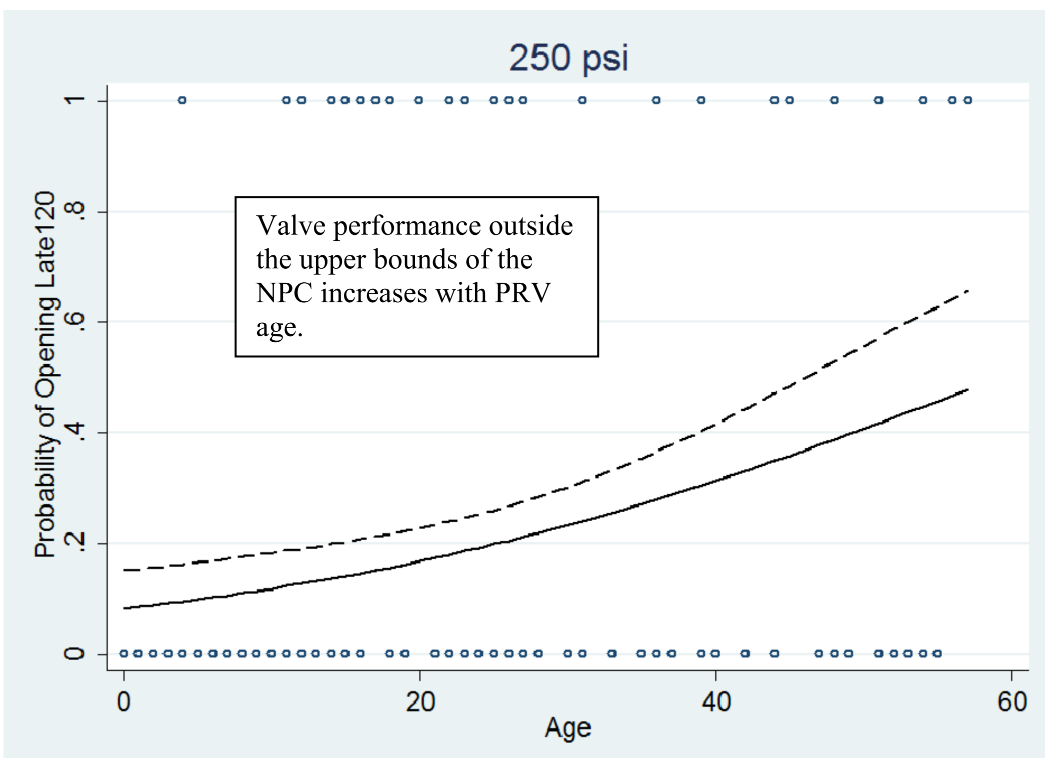

Figure 44. Estimated Probability and 95-Percent Upper Confidence Bound for Tendency to Open Late (120 percent) vs. Age (Years), 250-psig

5.0 Forensic Analysis

Battelle conducted forensic analyses for selected PRVs with STD pressures outside the bounds of the NPC to determine possible mechanisms and variables that may have contributed to the observed behavior. As stated previously, the performance criteria (NPC) 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 PRV selection process for forensic analysis involved reviewing the PRV STD data generated during this study to select a distribution of PRVs based upon their behavior during the performance testing; i.e., PRVs that did not open (DNO), PRVs that exhibited high STD pressure, and PRVs that exhibited low STD pressure. Multiple selection criteria were considered when selecting 24 PRVs for forensic analysis (>10 percent of the tested population). Battelle weighed several factors to determine which PRVs to consider in the forensic analysis. In approximate order of priority, those factors were:

1. PRVs that did not open by 375 psig
2. PRVs with performance issues noted during STD testing including leakage or other unexpected behavior
3. PRVs that exhibited very high or very low STD pressures.

While considering those factors, an effort was made to choose a set of PRVs that represented a variety of manufacturers, set pressures, sizes, and ages.

The examinations included observations of the conditions of the PRVs (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 PRVs once disassembled. As the PRVs 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 two PRVs that were 'stuck' closed (did not open by 375 psig), 18 PRVs that exhibited high STD pressures (greater than 120 percent of the set pressure), and 4 PRVs that exhibited low STD pressures (less than the set pressure). The PRVs selected for forensic analysis are presented in Table 2 and the detailed results are presented in the subsequent sections.

Table 2. PRVs Selected for Forensic Analysis

PRV INFORMATION						
PRV ID	**PRV Mfg ID**	**PRV Type**	**PRV Size (in)**	**PRV Age (yrs)**	**Performance Issue**	**STD Pressure (psig)**
250-psi Set Pressure PRVs						
96	A	I	¾	**4**	High STD	308
116	A	I	1	**16**	High STD	339
140	A	I	1¼	**15**	High STD	320
174	A	I	1	**44**	High STD	326
187	A	I	¾	**45**	Low STD – This PRV had a large leak between the gasket and body. The leak was large enough that the PRV could not complete the STD test protocol.	Leaked
395	A	I	¾	**31**	High STD	371
455	A	I	1	**15**	High STD	369
511	A	I	1	**26**	High STD	336
559	G	I	1	**44**	Low STD – PRV had a small leak between the stem and seal disc. The leak was noted, but small enough to complete STD testing of the PRV.	245
644	E	I	¾	**53**	High STD – This PRV was tested twice to 350 psig without opening (control program error terminated test at this pressure). On the third trial, the PRV opened at 254 psig.	254
660	A	I	1	**36**	High STD	325
674	F	I	1¼	**12**	High STD	344
696	A	I	1	**57**	High STD	352
699	A	I	1	**56**	High STD	353
750	A	I	¾	**27**	High STD	331
771	A	I	¾	**25**	High STD	312
780	A	I	1	**14**	High STD	337
275-psig Set Pressure PRVs						
122	C	I	1	**34**	DNO by 375 psig	DNO
523	A	I	1	**31**	High STD	341
593	A	I	1	**31**	High STD	335
597	C	I	¾	**40**	Low STD	194
650	A	I	1	**31**	High STD	342
733	D	I	¾	**50**	Low STD	197
760	C	I	1	**39**	DNO by 375 psig	DNO

5.1 PRV Spring Analyses

As part of the forensic 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, data from different PRV manufacturers were grouped together. The results of those measurements and evaluations are listed in Table 3.

In Table 3, 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 were 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.

Table 3. Spring Displacement and Load Data

PRV INFORMATION					PERFORMANCE ISSUE[a]	SPRING MEASUREMENTS		
PRV ID	PRV Mfg ID	PRV Type[b]	PRV Size (in)	PRV Age (yrs)		Spring Displacement (in)	Spring Load/ Displacement (lbs/in)	Spring Load (lbs)
250 psi Set Pressure PRVs								
Nominal Spring Wire Diameter = 0.155"; Disassembled Spring Length = 5.0"								
644	E	I	¾	53	High STD	0.921	151.3	139.4
Nominal Spring Wire Diameter = 0.159"; Disassembled Spring Length = 4.1"								
771	A	I	¾	25	High STD	0.630	220.9	139.0
Nominal Spring Wire Diameter =0.163"; Disassembled Spring Length = 4.1"								
96	A	I	¾	4	High STD	0.636	226.5	144.1
187	A	I	¾	45	Low STD, leak at gasket	0.636	211.3	134.4
395	A	I	¾	31	High STD	0.658	215.9	142.1

PRV INFORMATION					PERFORMANCE ISSUE[a]	SPRING MEASUREMENTS		
PRV ID	**PRV Mfg ID**	**PRV Type[b]**	**PRV Size (in)**	**PRV Age (yrs)**		**Spring Displacement (in)**	**Spring Load/ Displacement (lbs/in)**	**Spring Load (lbs)**
750	A	I	¾	26	High STD	0.607	218.0	132.3
Nominal Spring Wire Diameter = 0.167”; Disassembled Spring Length = 6.0 - 6.2”								
696	A	I	1	57	High STD	1.20	162.5	195.0
699	A	I	¾	55	High STD	1.22	159.4	194.4
174	A	I	1	42	High STD	1.13	153.6	173.9
Nominal Spring Wire Diameter = 0.186”; Disassembled Spring Length = 4.5”								
511	A	I	1	26	High STD	1.025	185.6	190.2
780	A	I	1	13	High STD	1.136	181.0	205.6
660	A	I	1	37	High STD	1.004	185.0	185.7
116	A	I	1	16	High STD	1.087	177.6	193.1
455	A	I	1	30	High STD	0.848	187.2	158.8
Nominal Spring Wire Diameter = 0.192”; Disassembled Spring Length = 4.5”								
559	G	I	1	45	Leaked Continuously	0.961	183.8	176.6
Nominal Spring Wire Diameter = 0.250”; Disassembled Spring Length = 4.75”								
140	A	I	1¼	17	High STD	0.959	360.8	346.0
Nominal Spring Wire Diameter = 0.250”; Disassembled Spring Length = 5.9”								
674	F	I	1¼	12	High STD	0.895	281.3	251.8
Spring 275 psi Set Pressure PRVs								
Nominal Spring Wire Diameter = 0.156”; Disassembled Spring Length = 5.0”								
597	C	I	¾	40	Low STD	0.806	158.5	127.8
Nominal Spring Wire Diameter = 0.164”; Disassembled Spring Length = 4.2”								
733	D	I	¾	50	High STD	0.651	207.1	134.8
Nominal Spring Wire Diameter = 0.186”; Disassembled Spring Length = 4.5”								
523	A	I	1	31	High STD	1.155	181.9	210.1
593	A	I	1	31	High STD	1.013	177.4	170.7
650	A	I	1	31	High STD	1.112	181.0	201.3
Nominal Spring Wire Diameter = 0.190”; Disassembled Spring Length = 7.0”								
122	C	I	1	34	DNO	1.096	173.5	190.2
760	C	I	1	39	DNO	0.925	204.8	189.1

(a) DNO = did not open; STD = start to discharge
(b) I = internal; E = external

There were few groupings of springs with essentially the same dimensions to make comparisons for the spring displacements, spring load/displacements, and resultant spring loads. As shown in Table 3, the data for one group of springs with a nominal spring diameter of 0.163 inch and spring length of 4.1 inches showed that two of the springs had very similar spring loads (144.1 and 142.1 pounds) but the other two springs had spring loads about 10 pounds less (132.2 and 134.4 pounds). Three of the PRVs (PRVs 96, 395, and 750) exhibited high STD pressures during testing but PRV 187 exhibited low STD behavior. The ages of the PRVs ranged from 4 to 45 years with no correlation between spring load and age.

For another group of springs with nominal spring wire diameters of 0.186-inch and disassembled spring lengths of 4.5 inches, the spring load/displacements ranged from 177.6 to 187.2 pounds/inch but because of differences in the loaded spring displacements the spring loads varied from 158.8 pounds to 205.6 pounds. The spring from PRV 455 exhibited the highest load displacement value but the lowest spring displacement and spring load. However, all of these PRVs exhibited high STD pressures. Thus the data in Table 3 do not explain the variations in the behaviors of the PRVs during pressure testing.

The calculated PRV spring loads were plotted versus the age of the PRVs in Figure 45 and Figure 46. The numbers next to the symbols in the chart represent the PRV identification number. Figure 45 and Figure 46 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 do not indicate that stress relaxation (load loss) contributed to the deterioration in PRV performance (did not open, high STD, or low STD) when pressure tested.

As shown in Figure 45 there was one PRV (PRV 140) that had a higher spring load (347 pounds) than the others. That spring also exhibited the highest load-displacement value. Additionally, the two PRVs with the highest spring loads (PRV 140 and 674) were 1¼-inch PRVs. The larger diameter valves would be expected to have higher spring loads, but the spring load (346 pounds) for PRV 140 seemed to be abnormally high in comparison to those from the other PRVs.

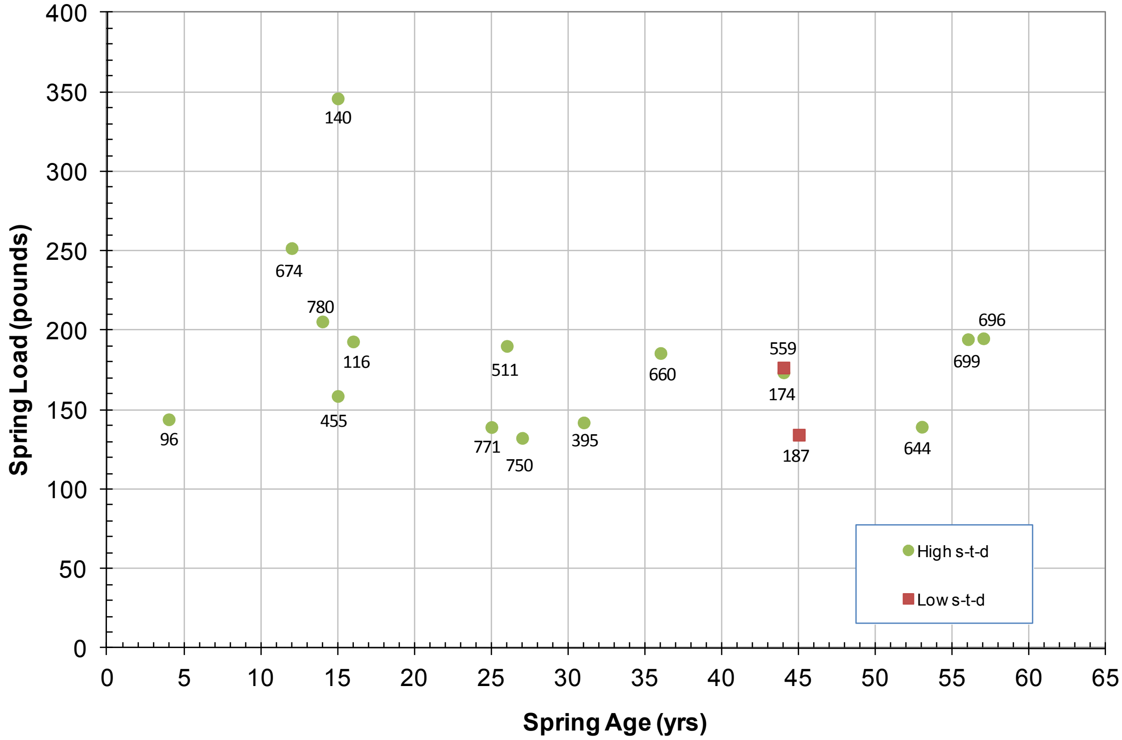

Figure 45. PRV Spring Load versus Age – 250-psig Set Pressure PRVs

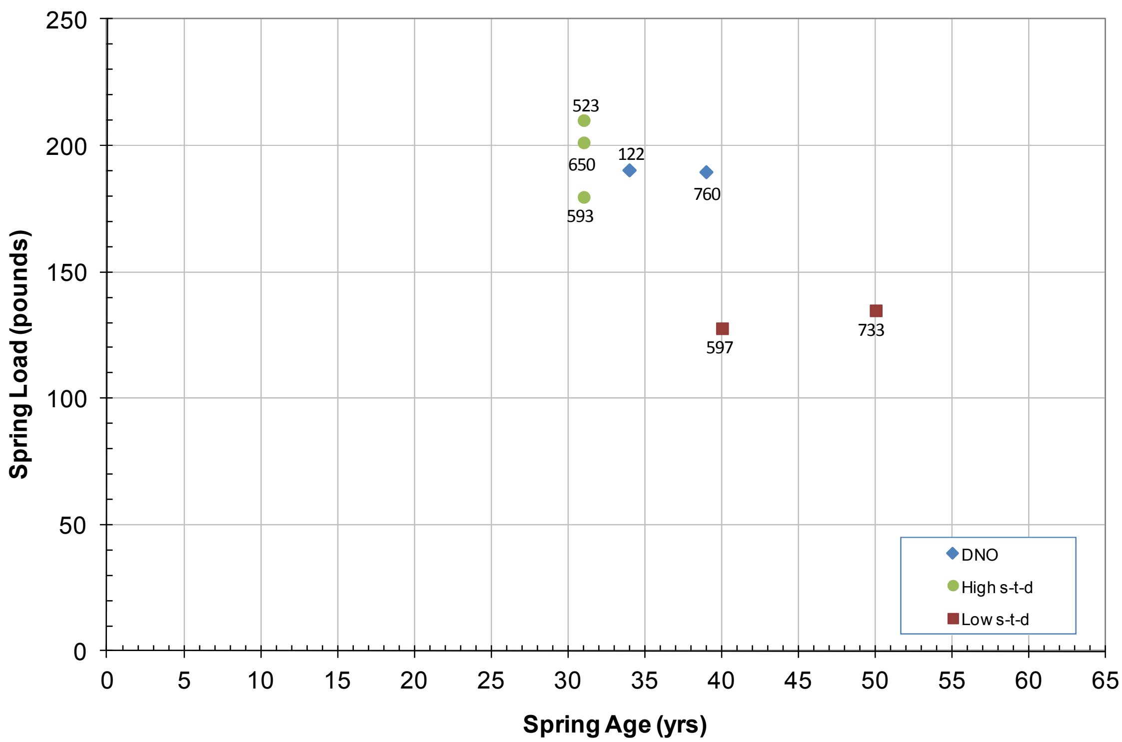

Figure 46. PRV Spring Load versus Age – 275-psig Set Pressure PRVs

5.2 Seat Disc (Gasket) Material Analyses

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. 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 PRVs were disassembled, the gasket in PRV 559 was stuck (bonded with adhesive) to the PRV housing. This PRV leaked continuously during testing but eventually discharged at 246.5 psig. The stem and holder in this PRV were different from any of the other PRVs that were examined. The stem was a long bolt that passed through the gasket holder and a small ring gasket was used to form the seal between the head of the stem and the gasket holder. Thus, the leaking and discharge of this PRV occurred at that small gasket rather than at the normal gasket/PRV body seal surface. The configuration of that PRV stem, gasket holder, and small gasket are shown in Figure 47 and Figure 48.

Figure 47. Slotted head on the Stem from PRV 559

Figure 48. Small Gasket on the Stem from PRV 559

The FT-IR analyses were carried out on the gaskets after they had been removed from the PRVs. The samples were analyzed using a Digilab FTS-7000e Fourier transform infrared spectrometer equipped with a Digilab UMA600 IR microscope. The data were acquired at 8 cm^{-1} spectral resolution. Samples were prepared by removing an outer layer of polymer to expose clean and (hopefully) un-degraded polymer. A thin slice of material was then removed and compressed into a thin film on a ZnSe IR window. Spectra were then obtained by transmission using the IR microscope.

Sample preparation of polymers that are filled with significant amounts of carbon black typically present a problem in IR analysis. The carbon black does not produce a spectrum per se, but rather absorbs the IR energy. This results in non-linear baselines and low transmittance values (in this case starting at around 5 percent transmittance as opposed to 100 percent). Commensurate with that, the IR bands used to identify the polymer are quite small and the spectra are noisy. However, the polymer bands in all cases for these samples were sufficiently intense that, with long scan times, the materials could be identified.

The gasket materials were identified by matching the IR spectra with those from known materials in IR libraries such as Bio-Rad Informatics “Know-It-All” software and other digital libraries. The results of the IR analyses, Shore D hardness measurements, and visual examinations of the gaskets are summarized in Table 4.

As is shown in Table 4, 21 of the 24 gaskets analyzed were identified to be butadiene-acrylonitrile commonly known as Buna N. The gaskets from PRVs 650 and 760 were identified as modified Butadiene-acrylonitrile copolymers. The gasket from PRV 650 also contained zinc ethylethiocarlomate and the gasket from PRV 760 was a partial but not exact match for the Butadiene-acrylonitrile copolymer; an exact compound match for the gasket from that PRV was not found. The gasket from PRV 674 was identified as Poly (vinylidene fluoride-co-hexafluoro propylene) which has the trade name Viton.

The Shore D hardness for the Buna N gaskets ranged from 38 to 64. That latter value may have been influenced by the fact that the gasket was thinner than the others and it was bonded to the brass gasket holder. Thus, the measured gasket hardness may have been raised by the hardness of the brass substrate. However, one of the other Buna N gaskets exhibited a Shore D hardness of 63. Both of the high hardness values were obtained from gaskets that were relatively old (44 years for the gasket from PRV 559 and 50 years old for the gasket from PRV 733.) However, Buna N gaskets from other PRVs of similar age did not exhibit elevated hardness.

Table 4. PRV Gasket Material Data

PRV INFORMATION					PERFORMANCE ISSUE[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 Pressure PRVs									
96	A	I	¾	**4**	High STD	Butadiene-acrylonitrile copolymer	Buna N	42	Compression set rings concentric, no obvious cracks in gasket, gasket loose in holder.
116	A	I	1	**16**	High STD	Butadiene-acrylonitrile copolymer	Buna N	51	Compression set rings not concentric, no obvious cracks in gasket, gasket loose in holder.
140	A	I	1¼	**15**	High STD	Butadiene-acrylonitrile copolymer	Buna N	50	Compression set rings not concentric, one radial crack in seal region, radial and circumferential cracks in outer circumferential ring.
174	A	I	1	**44**	High STD	Butadiene-acrylonitrile copolymer	Buna N	54	Compression set rings concentric, many radial cracks in outer circumferential ring; gasket stuck in holder and broke into many pieces when trying to remove it.
187	A	I	¾	**45**	Low STD (appeared to leak around the gasket during test)	Butadiene-acrylonitrile copolymer	Buna N	53	Compression set rings nearly concentric, rust deposited on surface of gasket, many radial and some circumferential cracks in outer circumferential ring, gasket material stuck to washer, gasket stuck to holder and started to break into pieces when removed.
395	A	I	¾	**31**	High STD	Butadiene-acrylonitrile copolymer	Buna N	54	Compression set rings not concentric, many radial cracks in outer circumferential ring; gasket stuck in holder and broke into many pieces when trying to remove it.

PRV INFORMATION					PERFORMANCE ISSUE[(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**
455	A	I	1	**15**	High STD	Butadiene-acrylonitrile copolymer	Buna N	53	Compression set rings not concentric, many radial cracks in outer circumferential ring; gasket stuck in holder and broke into several pieces when trying to remove it.
511	A	I	1	**26**	High STD	Butadiene-acrylonitrile copolymer	Buna N	49	Compression set rings not concentric, many radial and circumferential cracks in outer circumferential ring, gasket cracked when removed.
559	G	I	1	**44**	Leaked Continuously	Butadiene-acrylonitrile copolymer; small round gasket also was Butadiene-acrylonitrile copolymer	Buna N	64 (*)	Compression set rings concentric, no cracks in gasket, gasket was thin and stuck up above the holder surface and it was bonded to the brass holder.
644	E	I	¾	**53**	High STD	Butadiene-acrylonitrile copolymer	Buna N	41	Compression set rings concentric, no cracks in gasket; outer circumferential ring was dull (oxidized); gasket was loose in holder and was removed easily.
660	A	I	1	**36**	High STD	Butadiene-acrylonitrile copolymer	Buna N	51	Compression set rings not concentric, many radial cracks in the outer circumferential ring, that ring was dull (oxidized); some gasket material appeared to be pulled out of the seal region surface.
674	F	I	1¼	**12**	High STD	Poly (vinylidene fluoride-co-hexafluoro propylene)	Viton	16	Compression set rings not concentric, gasket seal surface region was dull and rust deposits were present, gasket appeared to have a dark coating and there was a crazed pattern (white lines) in the coating, gasket was loose in the holder and was easily removed.

PRV INFORMATION					PERFORMANCE ISSUE[(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**
696	A	I	1	**57**	High STD	Butadiene-acrylonitrile copolymer	Buna N	38	Compression set rings concentric, no cracks in the gasket; regions of material pullout from the seal surface region of the gasket. Outer circumferential ring was dull (oxidized).
699	A	I	¾	**56**	High STD	Butadiene-acrylonitrile copolymer	Buna N	45	Compression set rings not concentric, fine circumferential cracks in outer circumferential ring, ring of material pulled out of seal surface region of the gasket, gasket was loose in the holder and was removed easily.
750	A	I	¾	**27**	High STD	Butadiene-acrylonitrile copolymer	Buna N	45	Compression set rings nearly concentric, radial cracks in outer circumferential ring, that ring was dull (oxidized), gasket was loose in holder and was pliable but it broke into pieces when it was removed from the holder.
771	A	I	¾	**25**	High STD	Butadiene-acrylonitrile copolymer	Buna N	44	Compression set rings concentric, no cracks in gasket; outer circumferential ring was dull (oxidized); gasket was loose in the holder and was removed easily.
780	A	I	1	**14**	High STD	Butadiene-acrylonitrile copolymer	Buna N	39	Compression set rings not concentric, there appeared to be shallow circumferential cracks at the inner circumference of the seal surface region of the gasket, gasket was loose in the holder and was removed easily.

PRV INFORMATION					PERFORMANCE ISSUE[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**
275-psi Set Pressure PRVs									
122	C	I	1	**34**	DNO	Butadiene-acrylonitrile copolymer	Buna N	42	Compression set rings concentric, no cracks in gasket, gasket holder was magnetic and rusty (steel), rust on surface of gasket (probably was deposited during disassembly of the PRV), gasket was removed easily.
523	A	I	1	**31**	High STD	Butadiene-acrylonitrile copolymer	Buna N	52	Compression set rings not concentric, many radial cracks in outer circumferential ring, some radial cracks extended into the gasket seal surface region, gasket tore when removed.
593	A	I	1	**31**	High STD	Butadiene-acrylonitrile copolymer	Buna N	57	Compression set rings not concentric, no cracks in the gasket, outer circumferential ring dull (oxidized) and covered with debris, there were two regions where the gasket was not completely under the lip of the gasket holder, gasket was removed easily.
597	C	I	¾	**40**	Low STD	Butadiene-acrylonitrile copolymer	Buna N	45	Compression set rings not concentric, no cracks in gasket, outer circumferential ring was dull (oxidized) and rusty debris was present, gasket was removed easily.
650	A	I	1	**31**	High STD	Butadiene-acrylonitrile copolymer plus Zn ethylethiocarbamate	Buna N modified	52	Compression set rings nearly concentric, no cracks in gasket, outer circumferential surface was dull (oxidized) and contained some debris; gasket was removed easily.

PRV INFORMATION					PERFORMANCE ISSUE[(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**
733	D	I	¾	**50**	Low STD	Butadiene-acrylonitrile copolymer	Buna N	63	Compression set rings were concentric, one radial crack in the seal surface region, that ring was dull (oxidized), brass particles were present in the seal surface region of the gasket, gasket broke into many pieces when removed.
760	C	I	1	**39**	DNO	Most likely butadiene-acrylonitrile copolymer; no exact match found	Most likely Buna N	47	Compression set rings nearly concentric; no cracks in the gasket, rust on surface of outer circumferential ring; gasket holder was rusty and magnetic (steel); gasket was removed easily.

(a) DNO = did not open; STD = start to discharge
(b) I = internal; E = external
(*) The gasket was very thin and bonded to the gasket holder; consequently, the hardness values may have been affected by the gasket holder.

The Shore D hardness of the gaskets versus the age of the PRV is plotted in Figure 49 and Figure 50 for the 250-psig and 275-psig set pressure PRVs, respectively. Those plots show no trends of increasing or decreasing hardness with age. The low hardness value (Shore D 15) in Figure 49 was the Viton gasket from PRV 674.

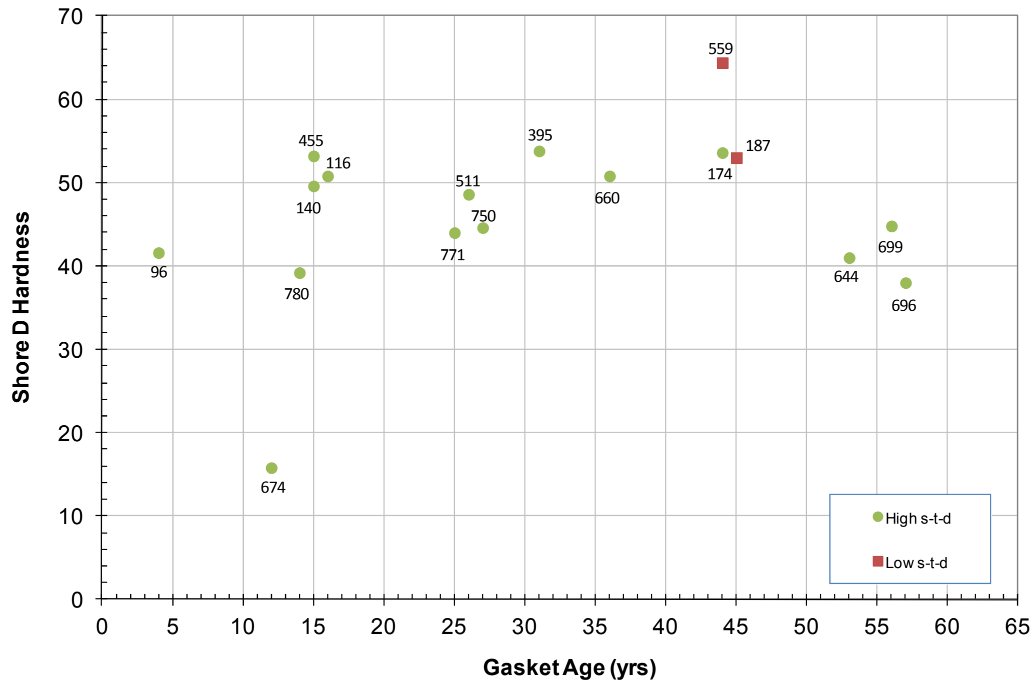

Figure 49. Shore D Hardness of the Gaskets vs Age from the 250-psig Set Pressure PRVs

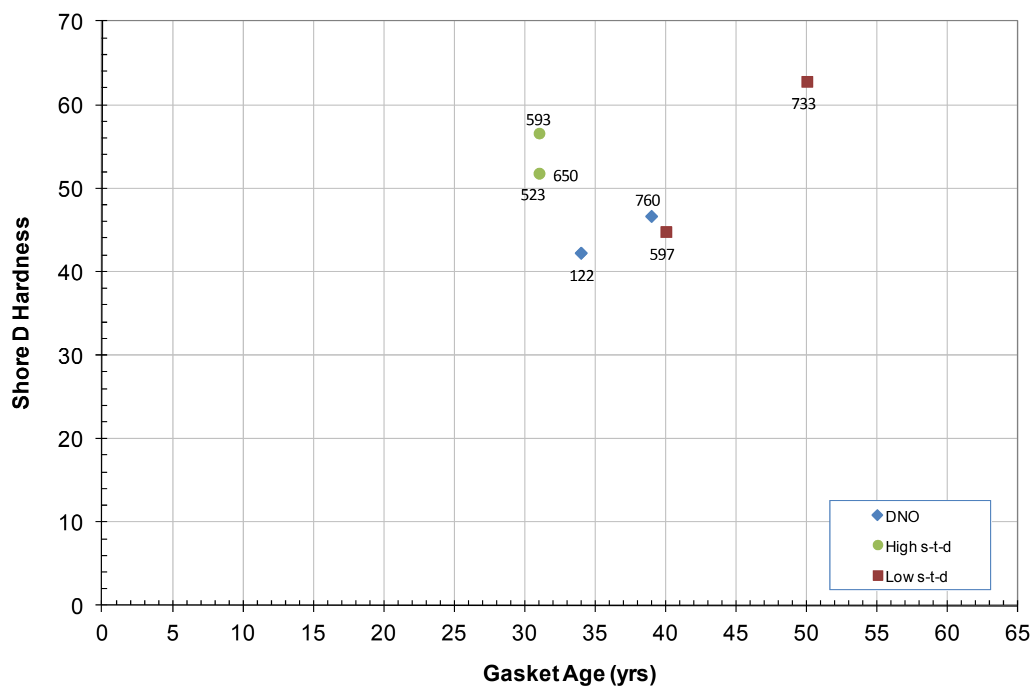

Figure 50. Shore D Hardness of the Gaskets vs Age from the 275-psig Set Pressure PRVs

Examination of the gaskets from the PRVs visually and under a low-power stereomicroscope revealed that all of them exhibited compression set rings. Those rings would be expected since the relatively soft gaskets were essentially statically loaded under hundreds of pounds of load for their service lives. On nine of the 250-psig set pressure PRVs and four of the 275-psig set pressure PRVs, the compression set rings were concentric indicating that the gaskets were centered in the PRV housings. Figure 51 illustrates the concentric compression set rings in the surface of the gasket from PRV 96. For the remainder of the PRVs (eight 250-psig set pressure and three 275-psig set pressure), the compression set rings were not concentric, indicating that the gaskets were not centered in the PRV housings. That condition could indicate possible misalignment of the PRV stem in the PRV. Figure 52 and Figure 53 illustrate the nonconcentric compression set rings in the gaskets from PRVs 116 and 174, respectively. However, this characteristic did not appear to significantly influence the PRV performance during pressure testing.

Figure 51. Concentric Compression Set Rings in the Gasket from PRV 96.

Figure 52. Nonconcentric Compression Set Rings in the Gasket from PRV 116.

The examinations of the gaskets also revealed that eleven of the 250-psig set pressure PRVs contained radial and /or circumferential cracks in the outer circumferential ring of the gasket. Only one of the gaskets from the 275-psi set pressure PRVs examined contained radial cracks in that region. Figure 53 shows multiple radial cracks in the outer circumferential ring of the gasket from PRV 174, in addition to the nonconcentric compression set rings. Figure 54 illustrates multiple circumferential cracks in the outer circumferential ring of the gasket from PRV 511. This gasket also contained radial cracks as are shown in Figure 55. The outer circumferential ring of the gasket is exposed to air during service and thus can become oxidized and discolored and often covered with other debris that gets inside the PRV housings, particularly when no rain caps are present. However, none of the cracks in the outer circumferential rings of the gaskets appeared to extend through the seal region of the gasket. Additionally, the gasket from PRV 559, which leaked continuously during testing, contained no cracks. Consequently, the presence of cracks in the outer circumferential rings of the gaskets does not explain why PRVs 187 and 559 leaked during pressure testing. Also, the cracks would not be expected to contribute to high STD pressures or to the PRVs not opening.

Figure 53. Nonconcentric Compression Set Rings and Multiple Radial Cracks in the Outer Circumferential Ring of the Gasket from PRV 174.

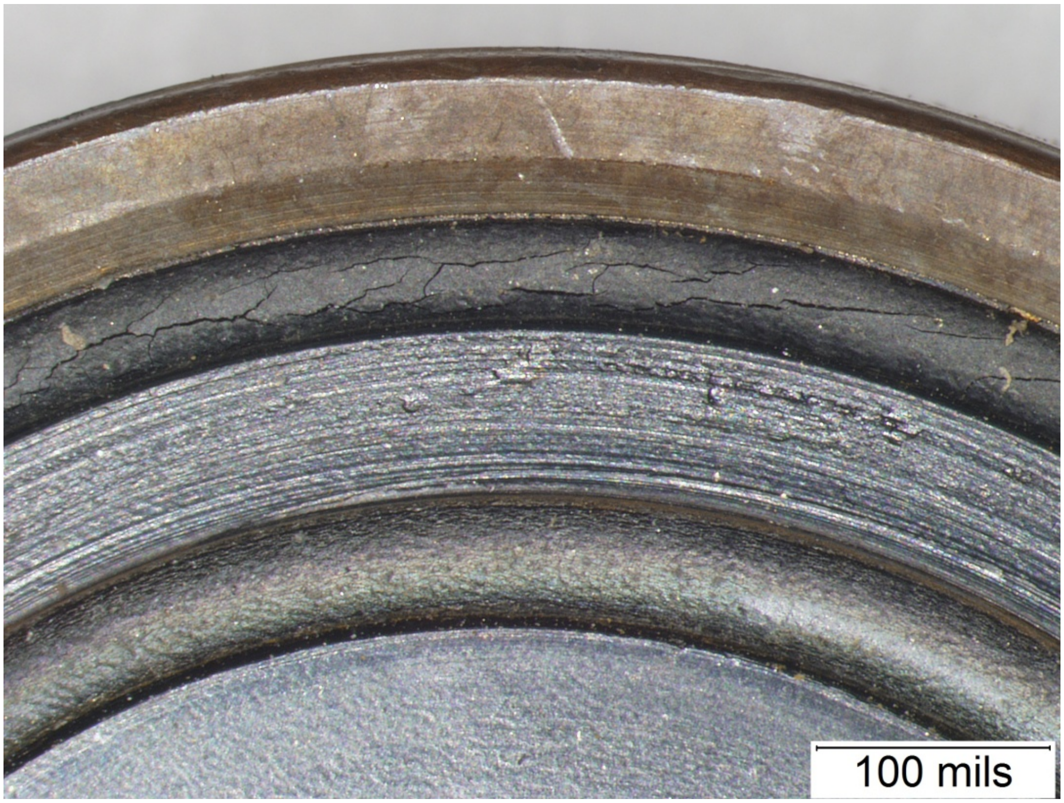

Figure 54. Multiple Circumferential Cracks in the Outer Circumferential Ring of the Gasket from PRV 511.

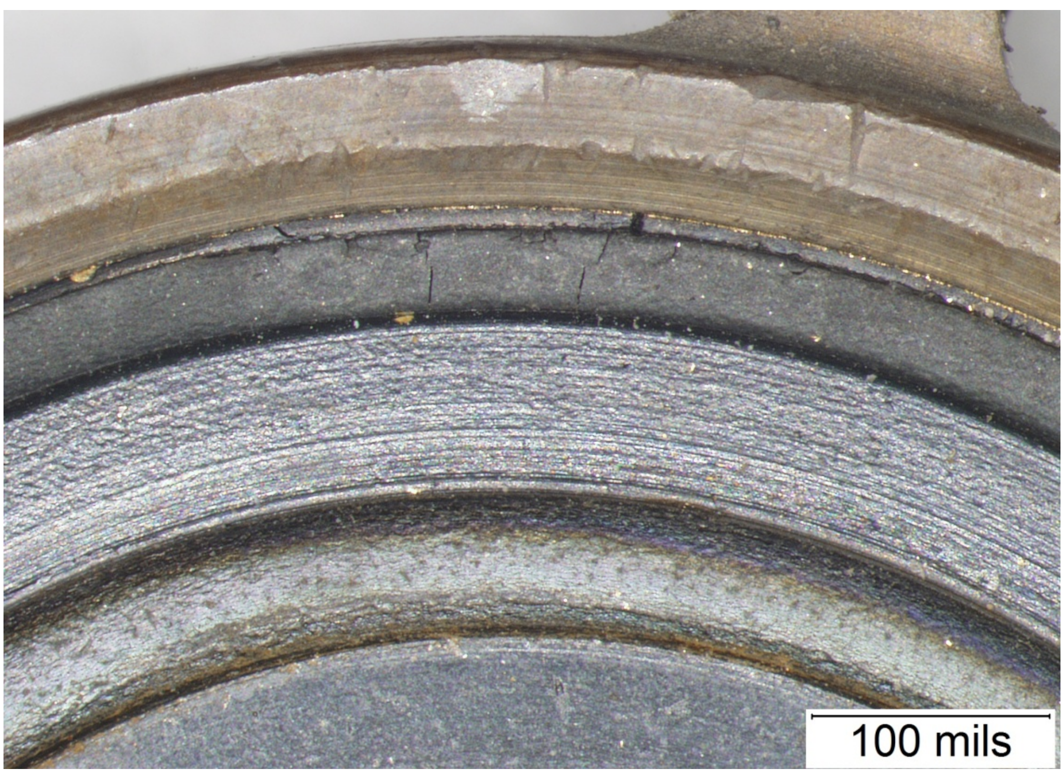

Figure 55. Radial Cracks in the Outer Circumferential Ring of the Gasket from PRV 511.

The gaskets from two of the PRVs, PRV 696 and PRV 699, exhibited evidence of material pull out and transfer of gasket material to the machined seal surface of the housing of the PRV. Figure 56 and Figure 57 shows the regions of material pull out from the seal surface of the gasket from PRV 696 at two different magnifications, respectively. Figure 58 shows the gasket material transferred onto the machined brass seal surface of the housing from PRV 696. It is possible that sticking of the gasket material may have contributed to the high STD pressure of the PRV.

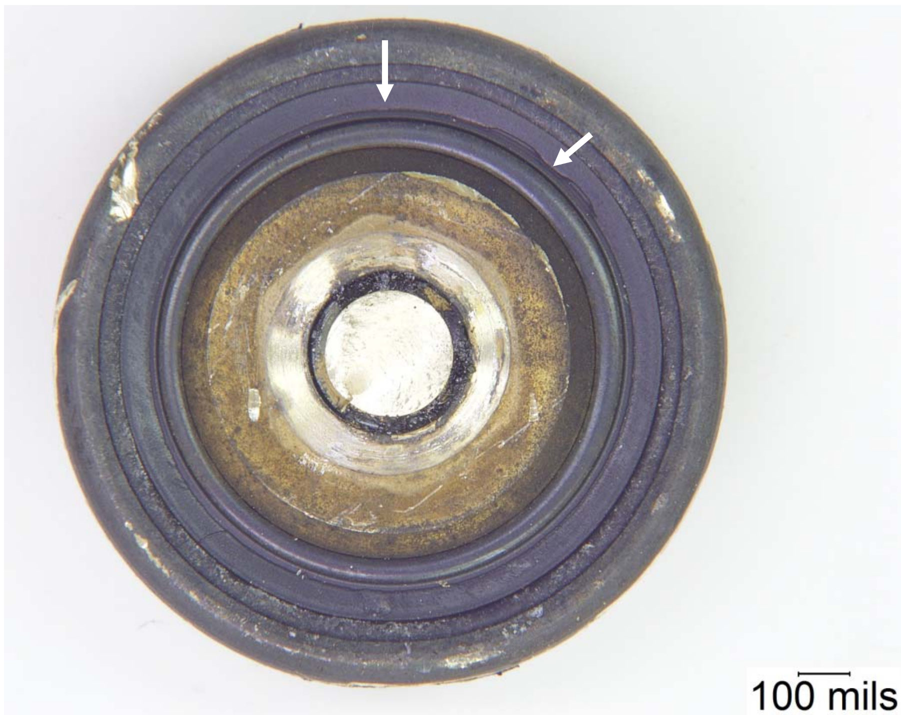

Figure 56. Material Pull (Arrows) Out from the Seal Surface Region on the Gasket from PRV 696.

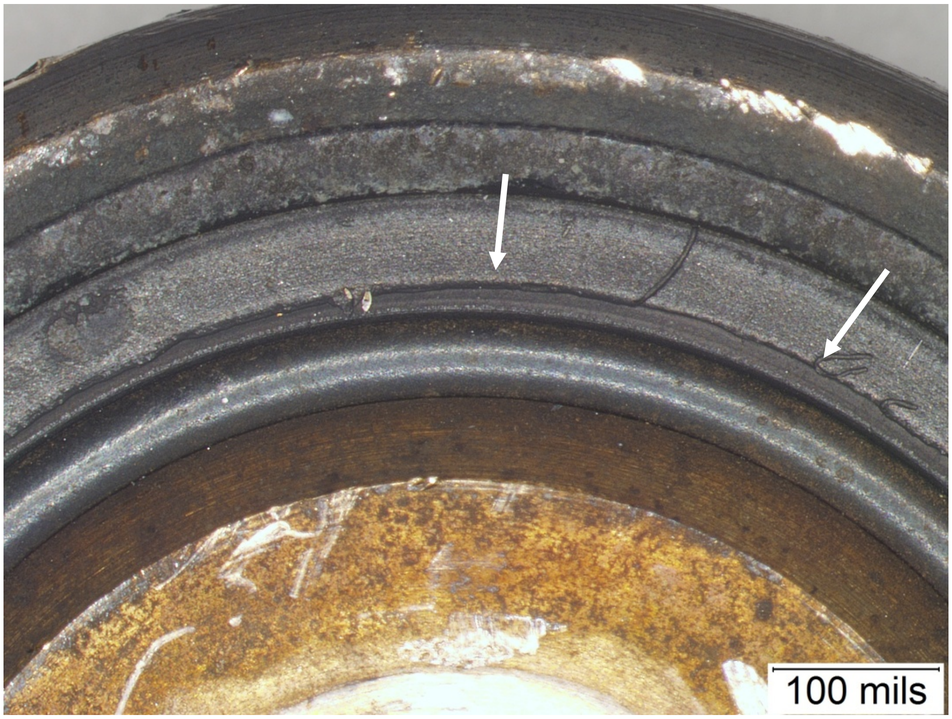

Figure 57. Higher Magnification view of a Region of Material Pullout (arrows) from the Seal Surface Region of PRV 696.

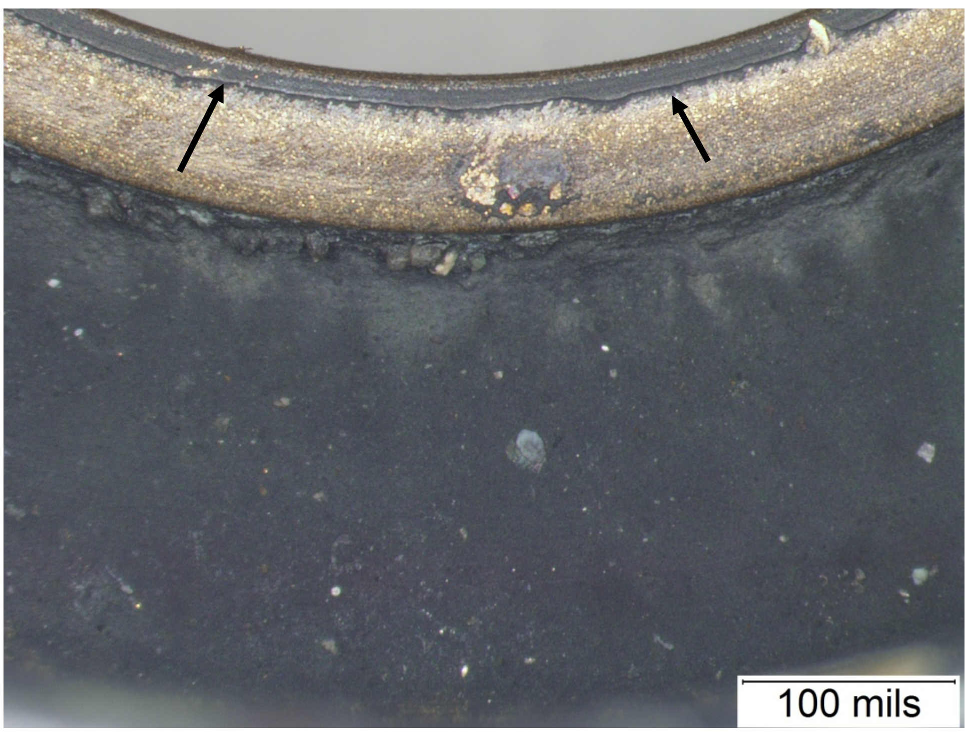

Figure 58. Material Transfer from the Gasket to the Machined Brass Seal Ring Surface (arrows) in the Housing from PRV 696.

The gasket from PRV 559 was different from those in the other PRVs. It was relatively thin, about 0.025-inches thick and bonded to the gasket holder. The thickness of the gasket shown in Figure 59 and Figure 60 shows the gasket holder after a portion of the gasket was cut from the holder using a razor blade. The Battelle investigators do not believe that these characteristics of the gasket contributed to the leaking of PRV 559 during pressure testing. They believe that the leakage occurred around the small ring gasket that was intended to form a seal between the PRV stem (long bolt shown previously in Figure 48) and the gasket holder.

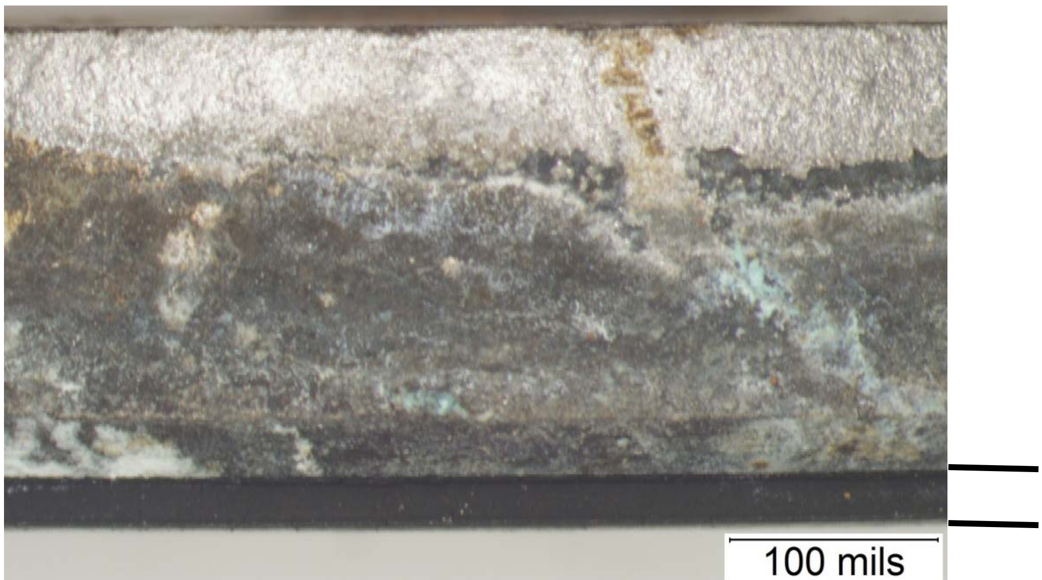

Figure 59. Thin Gasket on the Surface of the Gasket Holder from PRV 559.
The gasket was about 0.025-inch thick. The black lines indicate the thickness of the gasket.

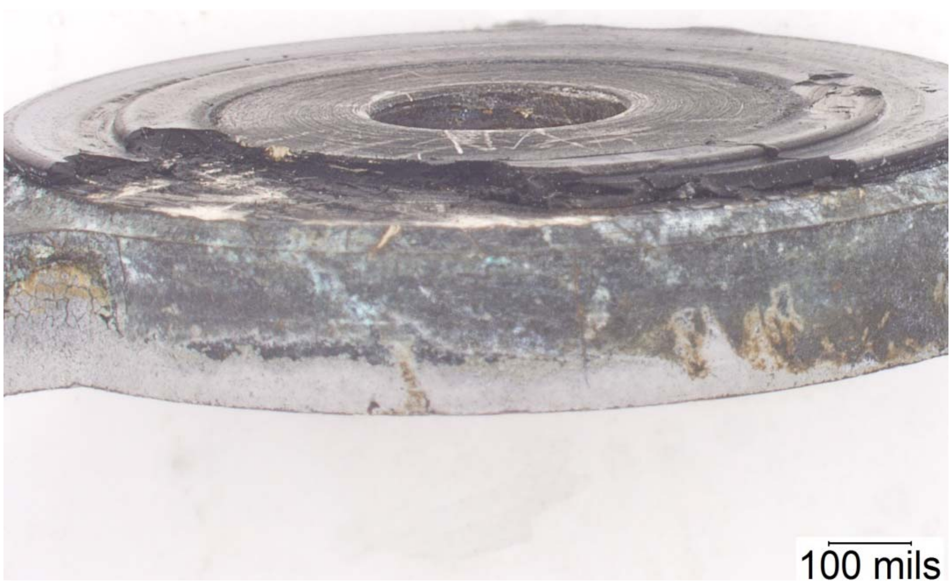

Figure 60. Gasket on the Surface of the Holder from PRV 559.
A portion of the gasket had been cut away with a razor blade.

The gasket from PRV 187, which appeared to leak around the gasket during pressure testing, was examined to determine if there was conclusive evidence of damage or other conditions that may have contributed to the leaking. The gasket surface is shown in Figure 61. As is shown, the surfaces of the gasket and the gasket holder were covered with a layer of rust. Those portions of the gasket were within the region of the PRV that was exposed to propane during service. As is shown in Figure 62, there were radial cracks in the outer circumferential ring of the gasket and rust particles on the seal surface region. However, neither the rust deposits nor the radial cracks confined to the outer circumferential ring appear to form a continuous leak path that would explain the leakage of this PRV.

Figure 61. Rust on the Surface of the Gasket and the Washer from PRV 187.
The rust was on the portion of the surface that was exposed to propane.

Figure 62. Higher Magnification View Showing Rust Particles on the Seal Portion of the Surface of the Gasket from PRV 187.
Note also the radial cracks in the outer ring of the gasket.

5.3 Rain Cap Issues

When the PRVs selected for analysis were examined visually, only two of the 24 PRVs had rain caps included with the PRV. However, the rain cap was frequently missing from the PRVs shipped to Battelle or separated from the PRV during STD testing. Thus, the lack of a rain cap for PRVs selected for forensic analysis did not mean that the rain cap was not present during service so the PRVs should be examined for evidence of a rain cap line on either the internal or external surface of the PRV fitting. Thus, all of the PRVs were examined for evidence of a rain cap line.

The results of the examination of the PRVs for the presence of a rain cap or a rain cap line are summarized in Table 5. Those results show that 16 of the 243 PRVs had evidence of either an internal or external rain cap line.

Table 5. Internal PRVs Rain Cap and Rain Cap Line Data

PRV ID	PRV Age (yrs)	PERFORMANCE ISSUE[(a)]	RAIN CAP PRESENT? YES/NO	RAIN CAP LINE PRESENT? YES/NO
250-psig Set Pressure PRVs				
96	4	High STD	Yes, external	Yes, external
116	16	High STD	Yes, internal	Yes, internal
140	15	High STD	No	Yes, faint internal
174	44	High STD	No	Yes, faint internal
395	31	High STD	No	No
455	15	High STD	No	Yes, faint internal
511	26	High STD	No	Yes, faint internal
559	44	Leaked Continuously	No	Yes, external
644	53	High STD	No	No
660	36	High STD	No	No, external surface has been buffed
674	12	High STD	No	Yes, external
696	57	High STD	Yes	Yes, internal
699	56	High STD	No	Yes, faint internal
750	27	High STD	No	Yes, faint internal
275-psig Set Pressure PRVs				
122	34	DNO	No	No
523	31	High STD	No	Yes, internal
593	31	High STD	No	Yes, faint internal
597	40	Low STD	No	No
650	31	High STD	No	Yes, faint internal
733	50	Low STD	No	No
760	39	DNO	No	No

(a) DNO – did not open; STD –start-to-discharge

Figure 63 shows PRV 96 and the external rain cap that accompanied the PRV. The arrows on Figure 63 point to the faint rain-cap line on the external surface of the PRV housing. Figure 64 shows PRV 116 and the internal rain cap that accompanied the PRV.

Figure 63. PRV 96 with External Rain Cap.
Note the faint rain-cap line (arrows) on the surface of the housing.

Figure 64. PRV 116 with an Internal Rain Cap.

Figure 65 and Figure 66 show the ribs that were molded on the surface of the internal rain cap and the resulting marks and rain-cap line on the internal surface of the housing from PRV 116. PRVs 455 and 523, which were not accompanied by internal rain caps, showed similar markings on the inside surfaces of their housings (see Figure 67 and Figure 68).

Figure 65. Ribs on the Surface of the Internal Rain Cap from PRV 116.
According to experienced personnel, even rain caps that remain in place on the PRV can curl up and allow rain to enter the PRV housing.

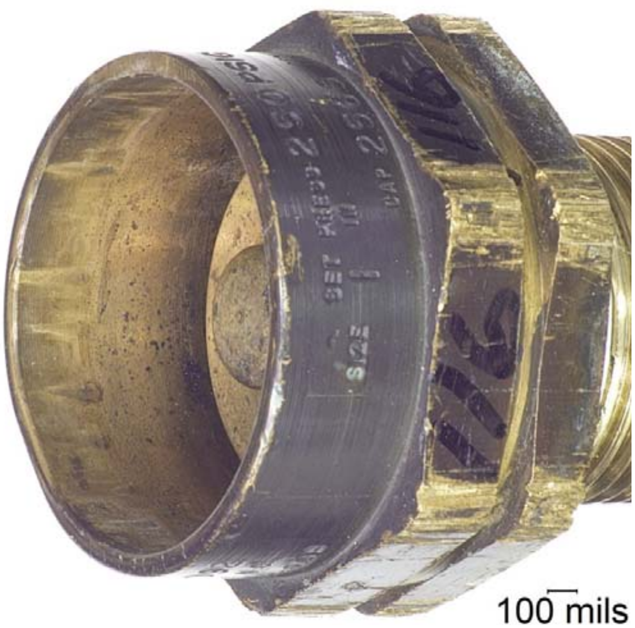

Figure 66. Rain Cap Line and Marks from the Ribs on the Rain Cap on the Internal Surface of the Housing from PRV 116.

As is shown in Figure 67, the white paint splotches and discoloration of the housing surface from exposure to the atmosphere in the region where the rain cap had been indicate that the rain cap likely had been in place for only a portion of the service life of the PRV.

Figure 67. Marks on the Inside Surface of the Housing from PRV 455 Indicating that an Internal Rain Cap had been Present for Only a Portion of the Service Life of the PRV.

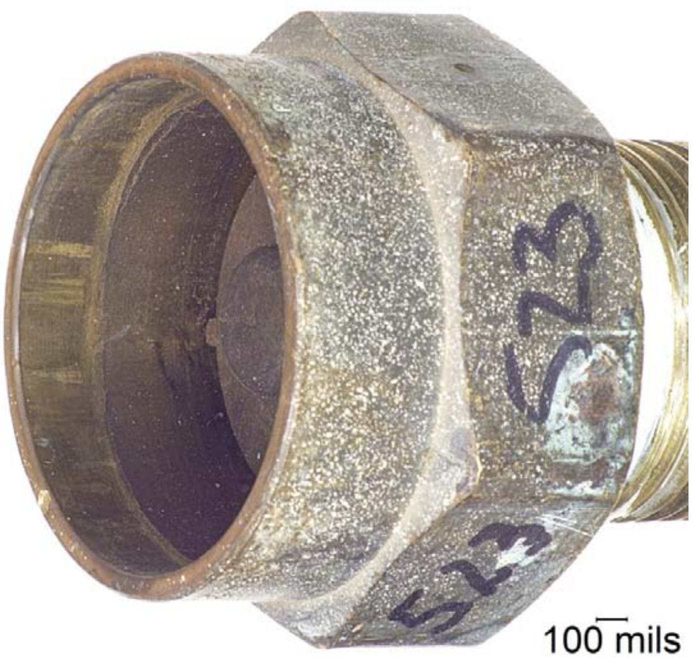

Figure 68. Internal Marks and Rain-Cap Line on the Internal Surface of the Housing from PRV 523.

Figure 69 illustrates a faint rain cap line on the internal surface of the housing from PRV 140. The discoloration of the housing surface outboard from the rain-cap line indicates that the rain cap may have been present for only a portion of the service life of the PRV.

Figure 69. Faint Internal Rain-Cap Line on the Housing from PRV 140.

Figure 70 illustrates a very distinct rain-cap line on the external surface of the housing from PRV 674. That figure also shows a band discoloration and corrosion on the inner surface of the housing just below the top of the PRV. The presence of that band is puzzling considering the lack of discoloration and corrosion on the external surface of the housing.

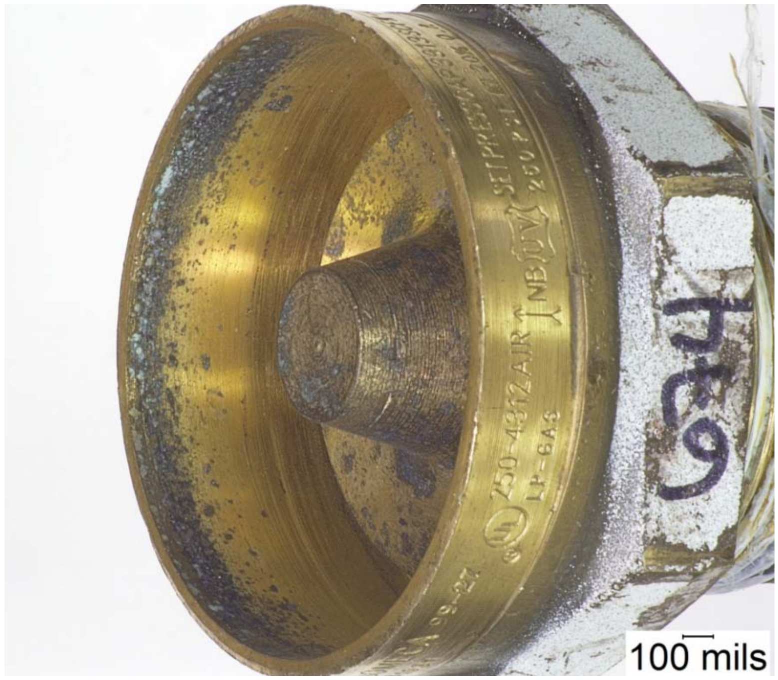

Figure 70. Distinct External Rain-Cap Line on the Surface of the Housing from PRV 674.

Figure 71 and Figure 72 show two of the PRVs that exhibited no conclusive evidence of a rain-cap line on either the internal or external surfaces of the PRV housing. Figure 71 also shows that the external surface of the housing had been painted and some of the paint had run over onto the inside surface.

Figure 72 shows that the surface of the gasket holder inside the PRV housing from PRV 760 was severely corroded. That gasket holder was magnetic and thus most likely was fabricated from a carbon or low alloy steel. The absence of a rain cap allowed the environment to contact and corrode the gasket holder. PRV 122 also showed no evidence of a rain-cap line and the gasket holder from that PRV also was magnetic and severely corroded. It appeared that the gasket holders in all of the other PRVs were fabricated from brass. PRVs 122 and 760 were produced by the same manufacturer and were the only PRVs that did not open during pressure testing.

The Battelle investigators strongly recommend that more attention to the presence of rain caps and clear weep holes be given by tank users and tank service personnel. If a rain cap is found to be missing during service, a new one should be installed. Keeping a rain cap in place should minimize debris from entering the PRV and also reduce corrosion. If a weep hole is found to be plugged during service, it should be cleared to prevent a build-up of moisture inside the valve housing which also will reduce corrosion.

Figure 71. Housing from PRV 597 Showing no Evidence of Internal or External Rain-Cap Lines.

Figure 72. Housing from PRV 760 Showing no Evidence of Internal or External Rain-Cap Lines.
Note the severe corrosion on the surface of the gasket holder.

5.4 Summary of Forensic Analyses

5.4.1 PRVs That Did Not Open

The two PRVs that did not open were PRV 122 and PRV 760. Both PRVs were identical models produced by Manufacturer C. A third PRV of similar age and identical manufacturer and model was tested and found to open within the NPC bounds. PRV 122 was 34 years old and PRV 760 was 39 years old. Examinations of these two PRVs showed many similar features, which will be described in the subsequent paragraphs.

Figure 73 and Figure 74 show PRV 122 and PRV 760, respectively, as they were received for the forensic investigation. The spring on PRV 122 had a gold tint but showed little evidence of corrosion, except near the bottom of the spring adjacent to the set pressure locking nut. There was some corrosion on the surface of the locking nut and the threaded position of the stem that extended beyond the locking nut. The locking nut appeared to be soldered to the PRV stem. The spring from PRV 760 was silver colored and showed no evidence of corrosion. The locking nut appeared to be soldered to the PRV stem and there was a slight amount of corrosion on the surface of the locking nut.

The guide spacers between the fitting and the spring washer were tubes that had three gussets that fanned out to a flange that contacted the bottom of the PRV housing. These spacers were about 2 inches long and the surfaces were significantly discolored. However, the washers on top of the springs in both PRVs were not discolored. Battelle investigators did not know whether or not the spacer guides had been treated to form the dark coating prior to assembling the PRVs.

Figure 73. Overall View of PRV 122 (275-psig Set Pressure) that Did Not Open During Pressure Testing. *Note the bow in the spring.*

Figure 74. Overall View of PRV 760 (275-psig Set Pressure) that Did Not Open During Pressure Testing. *Note the slight bow in the spring.*

The internal and external surfaces of the housings from these PRVs were discolored and showed no evidence of any rain-cap lines. There was debris inside the housings. In addition, the surfaces of the gasket holders were covered with rust. These features are shown in Figure 75 through Figure 77.

Figure 75. Discoloration of the Inside Surface of the Housing, Debris Inside the Housing, and Rust on the Surface of the Gasket Holder from PRV 122

Figure 76. Additional Debris on the Inside Surface and the Absence of Rain-Cap Lines on the Internal and External Surfaces of the Housing from PRV 122.

Figure 77. Discoloration of the Internal Surface of the Housing, Debris Inside the Housing, and Rust on the Surface of the Gasket Holder from PRV 760.

When the PRVs were disassembled, the solder at the locking nut was removed with a small grinder. The locking nut was then turned to remove it. During this operation the stems of the PRVs turned and came out of the gasket holders. However, the stems could not be removed from the PRV housings and guide fittings. The PRVs were then placed in an Instron universal testing machine and the stems were pushed to remove them from the PRV housings.

During that testing, the stem in PRV 122 began to move at an applied load of 57.2 pounds, but to continue to move the stem, the load increased to 151.9 pounds. Even after the stem moved several inches out of the housing, it was still tight in the housing and the guide spacer could not be removed by hand. Figure 78 shows the stem partially pushed out of the housing. That figure also shows that the surface of the stem was dull but not corroded. Figure 78 also shows bright rub mark regions on the surface of the stem. Figure 79 shows those rub marks at higher magnification. Those marks most likely formed when the stem turned in the guide spacer when the PRV was being disassembled.

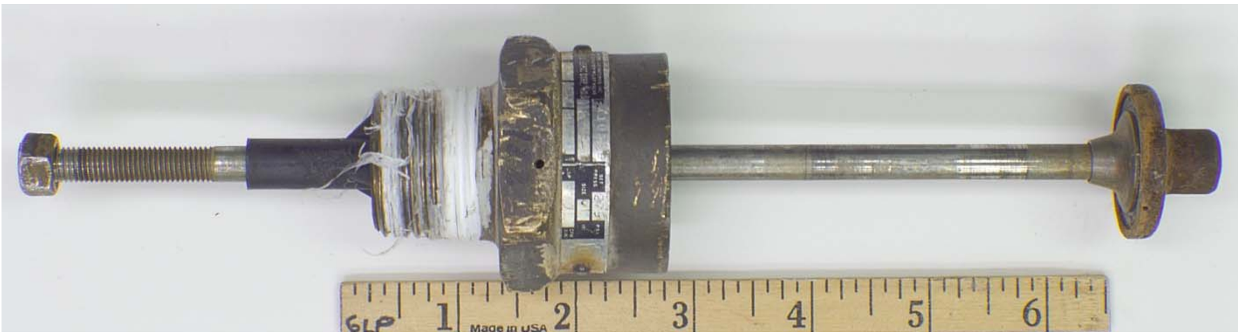

Figure 78. Stem Partially Pushed Out of the Housing from PRV 122.
The shiny marks on the stem were caused when it turned during disassembly.

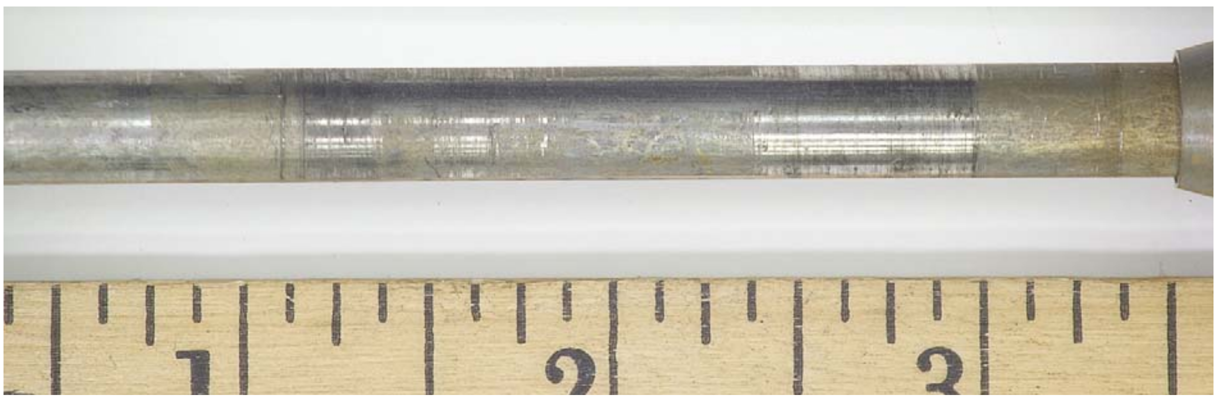

Figure 79. Circumferential Rub Marks on the Surface of the Stem from PRV 122.
The rub marks were caused when the stem turned during disassembly.

The load required to move the stem in the guide spacer from PRV 760 was only 22.7 pounds. Once the movement started the stem could be pushed out of the guide spacer by hand with some effort; but it was not loose. Figure 80 shows the stem from PRV 760 after it was removed. Rub marks were present on the stem surface similar to those that were on the stem from PRV 122; those marks are shown at higher magnification in Figure 81. Both Figure 80 and Figure 81 show that the surface of the stem was not corroded.

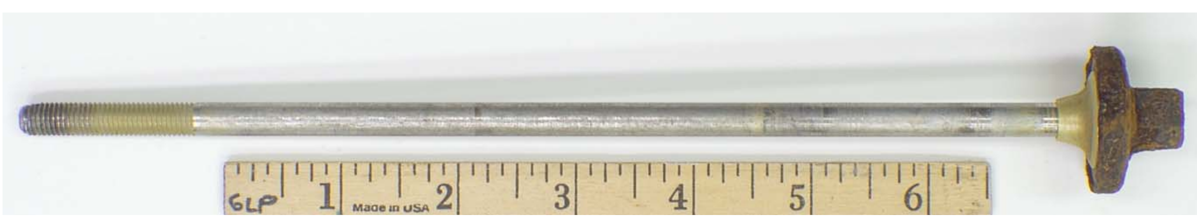

Figure 80. Appearance of the Stem After it was Pushed Out of the Housing from PRV 760.

Figure 81. Circumferential Rub Marks on the Surface of the Stem from PRV 760.
The rub marks were caused when the stem turned during disassembly.

Figure 82 and Figure 83 show the gaskets in the severely corroded gasket holders from PRV 122 and PRV 760, respectively. As was reported previously, these gaskets were not stuck to the seal surfaces in the PRV housings and there was no evidence of gasket material transfer to those housings. The magnetic responses of the gasket holders were checked and they were found to be magnetic. Thus, they were produced from carbon or low alloy steels. The gasket holders from the other PRVs examined appeared to be made from brass. In addition, the magnetic response of the stems from these PRVs was checked and they were found to be magnetic. Thus the stems were fabricated from a carbon or low alloy steel. However, they were not exposed to the corrosive environments like the gasket holders.

Based upon the examination of PRV 122 and PRV 760 that did not open by 375 psig during pressure testing, the Battelle investigators believe that the reason for the observed behavior was that the stems had become 'stuck' to the guide fittings during service even though significant corrosion did not occur between those surfaces.

Figure 82. Rusted Bottom Surface of the Gasket Holder and Debris on Seal Surface Region of the Gasket from PRV 122.

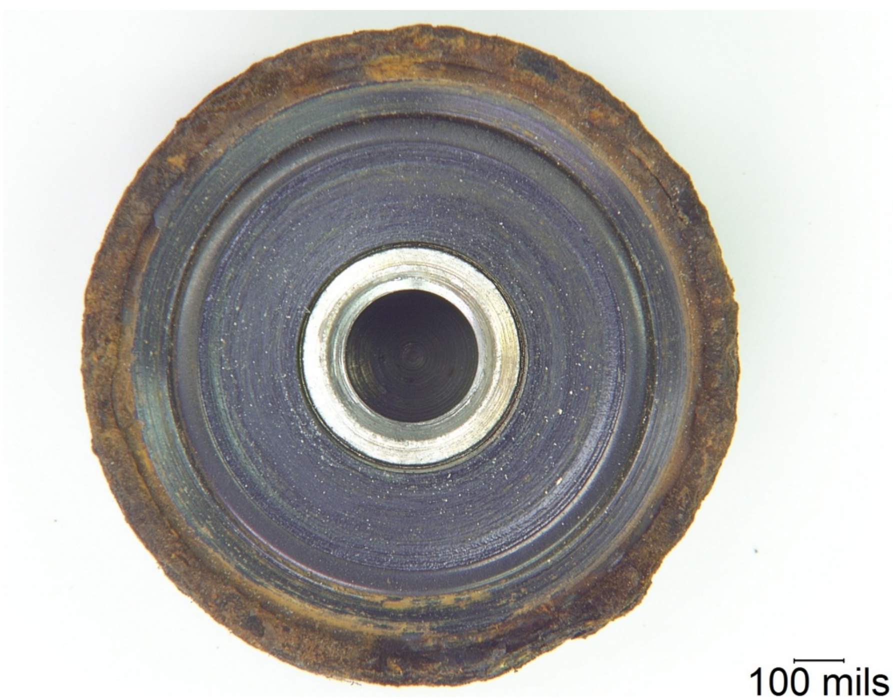

Figure 83. Severely Corroded Bottom Surface on the Gasket Holder from PRV 760.

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

Fifteen of the 250-psig set pressure PRVs and three of the 275-psig set pressure PRVs exhibited high STD pressures. All of these PRVs were examined visually and disassembled for more detailed examinations to determine to the extent possible the most probable cause for the high STD pressure behavior.

Examination of those PRVs revealed that most of them showed relatively little evidence of deterioration as a result of their service lives. The one high STD PRV that exhibited the most extensive corrosion on its exposed components was PRV 674 which had been in service for 53 years. This PRV was tested twice to 350 psig without opening; on the third pressurization cycle the PRV opened at 254 psig, very near the set pressure for the PRV.

Figure 84 shows the overall view of PRV 674. This figure shows the whitish corrosion products on the spring, the dark corrosion products on the spacer guide, and corrosion on the stem below the set pressure lock nut. Surprisingly, the external surface of the fitting showed little discoloration and there was little corrosion on the inside surface of the housing and the gasket holder. These features are shown in Figure 85 and Figure 86. This PRV apparently had an external rain cap in place for most of its service life. Figure 87 shows extensive corrosion products ('white' and red rust) on the surface of the PRV stem and dark corrosion products on the spacer guide surfaces. Figure 88 and Figure 89 illustrate more corrosion products on the surface of the stem and the gasket washer.

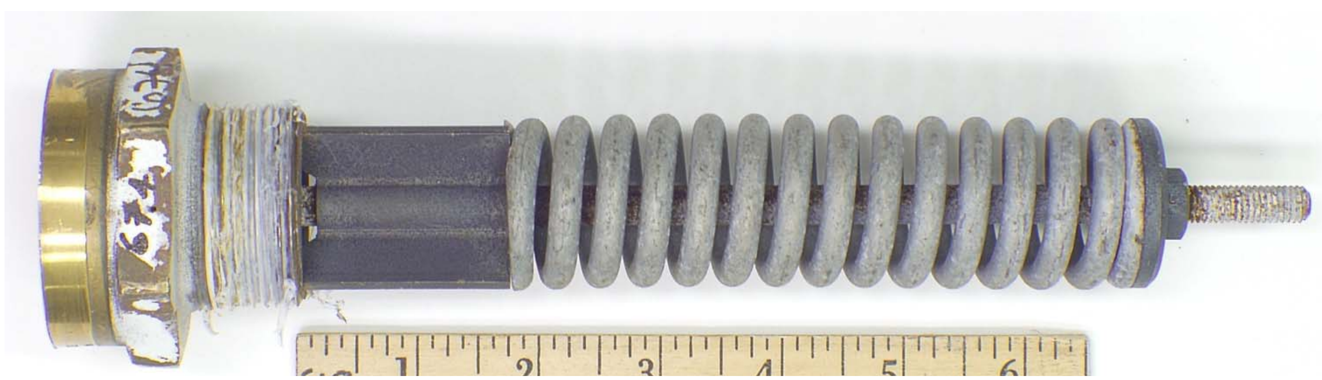

Figure 84. Overall View of PRV 674, 250-psig Set Pressure PRV that Exhibited High STD Behavior.

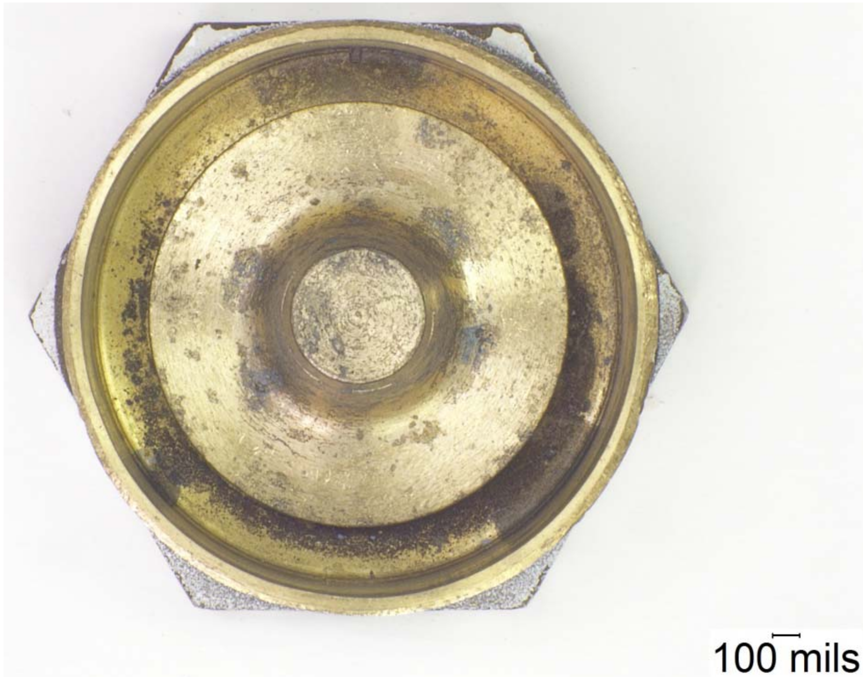

Figure 85. Slight Discoloration of the Inside Surface of the Housing and the Gasket Holder from PRV 674.

Figure 86. Lack of Discoloration and Corrosion on the External Surface of the Housing but a Band of Corrosion Near the Top of the Internal Surface from PRV 674.

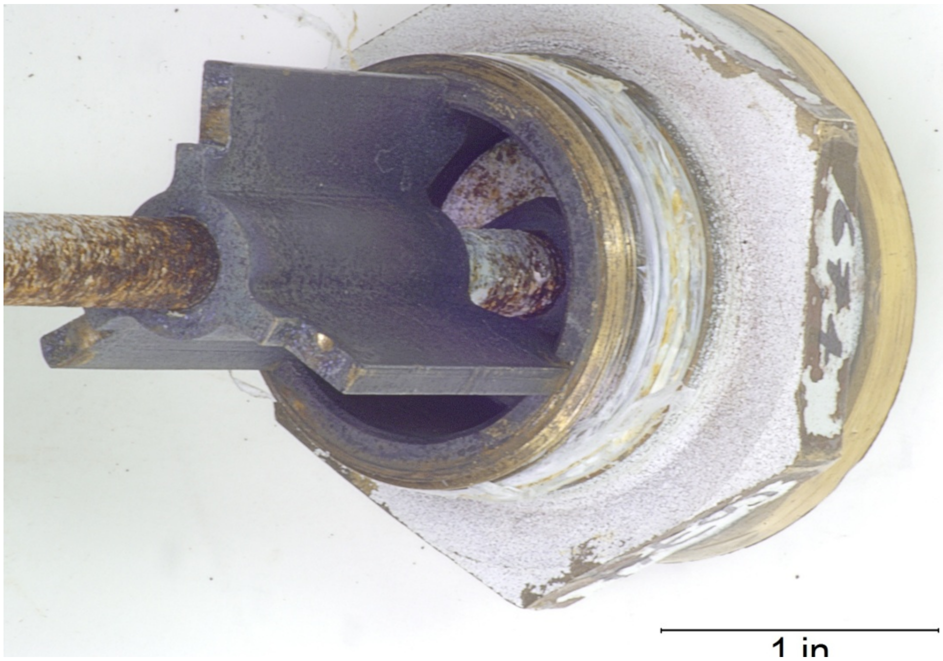

Figure 87. Corrosion Products (Red Rust and "White" Rust on the Surface of the Stem and Black Corrosion Products on the Surface of the Spacer Guide) from PRV 674.

Figure 88. Mixed-Color Corrosion Products on the Surface of the Stem from PRV 674.

Figure 89. Mixed-Color Corrosion Products on the Surface of the Gasket Washer from PRV 674.

When the PRV was disassembled, the stem was stuck in the spacer guide and PRV housing. The stem was pushed out of the housing and spacer guide using an Instron Universal Testing machine. The load required to get measurable movement of the stem was 968.2 pounds (displacement was 0.015-inches). The load then dropped to between 500 and 600 pounds to move the stem. Based upon those measurements, it is difficult to understand how the PRV discharged at 254 psig during the third pressurization cycle.

A magnetic check revealed that the stem was magnetic and energy dispersive spectroscopy (EDS) analysis of a piece of the stem revealed that it was a low alloy steel that contained about 1.3 percent chromium, 0.9 percent manganese, and 0.4 percent silicon. X-ray diffraction analyses of the corrosion products on the stem of PRV 674 revealed the presence of magnetite (iron oxide), hydrozincite, and ashoverite (zinc hydroxide). Those results indicate that the stem was made from a low alloy steel that had been zinc coated, most likely electroplated.

The Battelle investigators concluded that the high STD behavior of PRV 674 was caused by the corrosion of the stem and spacer fitting that was exposed to the environment inside the propane tank. This type of corrosion indicates that there was a significant amount of moisture inside the tank. The voluminous corrosion products formed on the sacrificial anode zinc coating would be expected to contribute to sticking of the stem, and thus, PRVs of this design may pose problems in service.

None of the other PRVs that exhibited high STD behavior during testing exhibited the extent of corrosion to their components as did PRV 674. However, all of them did exhibit a distinct mark on the PRV stem formed by contact between the PRV stem and the spacer guides. Figure 90 through Figure 107 show the contact marks on the PRV stems from PRVs 96, 116, 750, 395, 523, and 644. These PRVs ranged in age from four to 53 years. As shown in these figures, the PRVs showed little or no corrosion on the various components. In addition, none of the PRVs exhibited evidence of sticking of the gaskets when they were disassembled. Consequently, the Battelle investigators conclude that the most likely reason for their high STD behavior was the sticking of the PRV stem to the guide spacers or guide washers. The other high STD PRVs except PRV 674 and PRV 696 showed similar characteristics. As was discussed previously, PRV 674 exhibited significant corrosion on the PRV stem.

Figure 90. PRV 96, 250-psig Set Pressure, that Exhibited High STD Behavior.
This PRV was four years old.

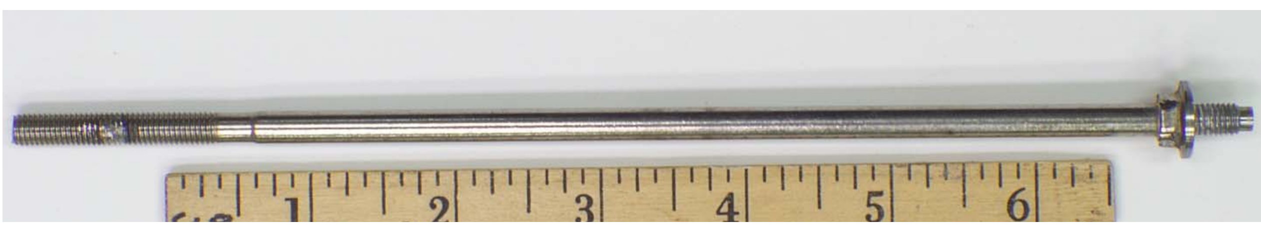

Figure 91. PRV Stem for PRV 96.

Figure 92. Mark on the Stem Formed by Contact between the PRV Stem and the Guide Spacer/Washer from PRV 96.

Figure 93. PRV 116, 250-psig Set Pressure PRV that Exhibited High STD Behavior. ***This PRV was 16 years old.***

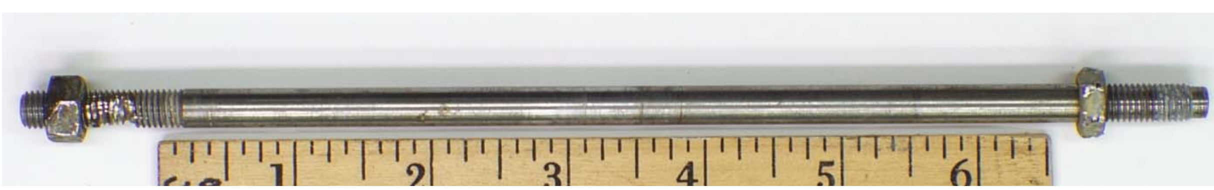

Figure 94. Stem from PRV 116.

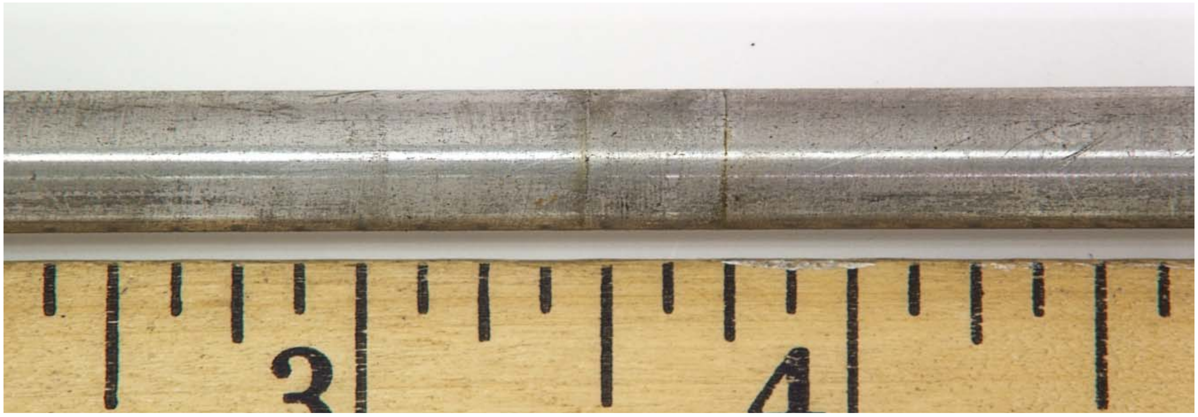

Figure 95. Mark on the Stem Formed by Contact Between the PRV Stem and the Guide Washer from PRV 116.

Figure 96. PRV 750, 250-psig Set Point PRV that Exhibited High STD Behavior.
This PRV was 27 years old.

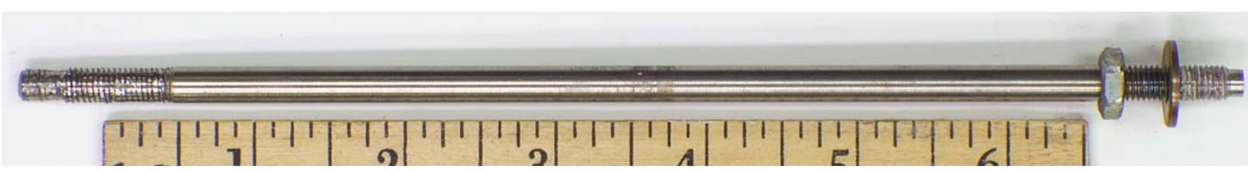

Figure 97. Stem from PRV 750.

Figure 98. Mark on the Surface Formed by Contact Between the PRV Stem and the Guide Washer from PRV 750.

Figure 99. PRV 395, 250-psig Set Pressure PRV that Exhibited High STD Behavior.
This PRV was 31 years old.

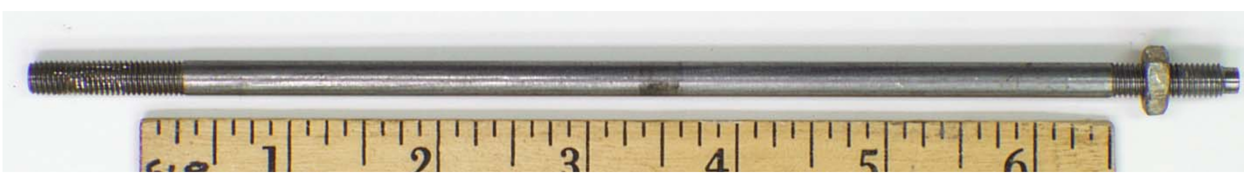

Figure 100. PRV Stem from PRV 395.

Figure 101. Mark on the Surface Formed by Contact Between the PRV Stem and the Spacer/Guide from PRV 395.

Figure 102. PRV 523, 275-psig Set Pressure PRV that Exhibited High STD Behavior.
This PRV was 31 years old.

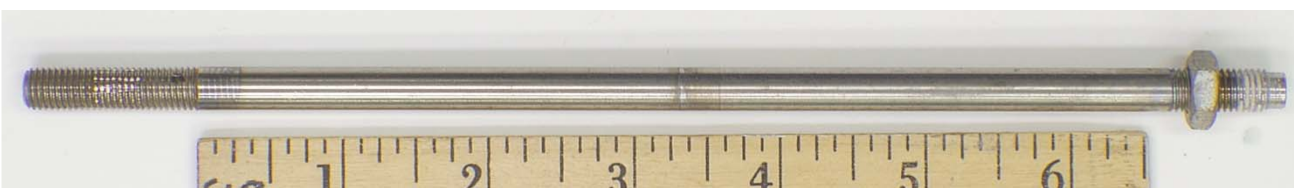

Figure 103. PRV Stem from PRV 523.

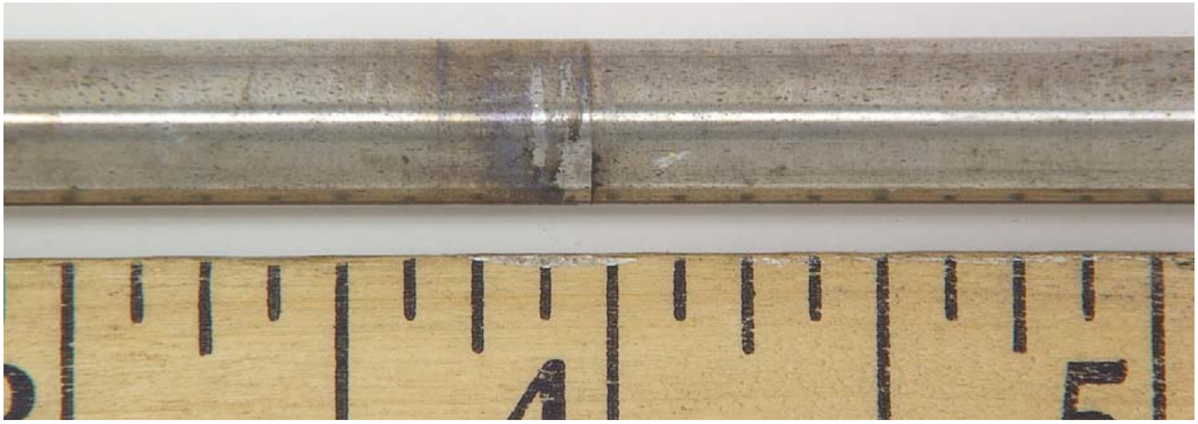

Figure 104. Mark on the Surface Formed by Contact Between the PRV Stem and the Guide Washer from PRV 523.

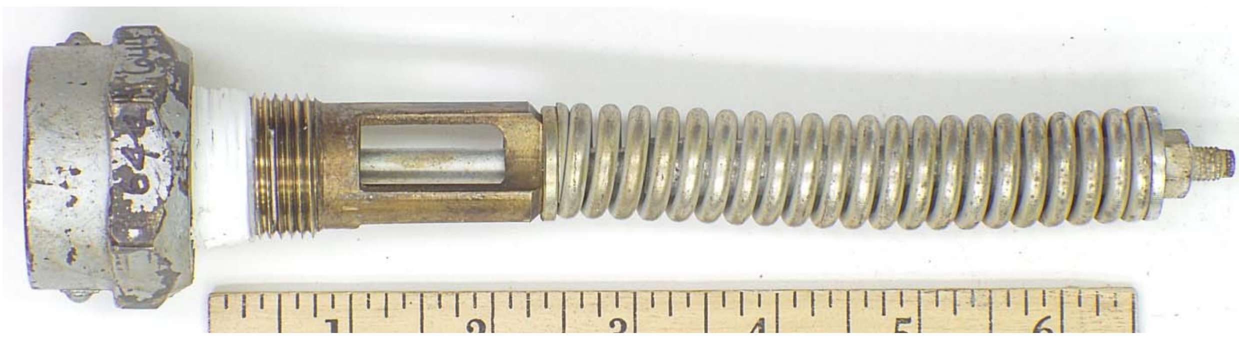

Figure 105. PRV 644, 250-psig Set Pressure PRV that Exhibited High STD Behavior.
This PRV was 53 years old. Note the bow in the spring.

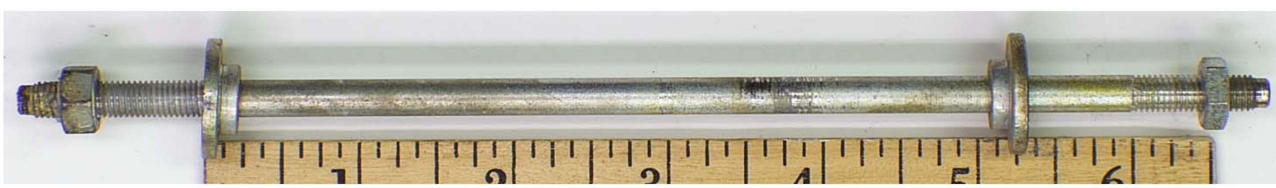

Figure 106. PRV Stem from PRV 644.
Note the light discoloration/corrosion beyond the contact mark.

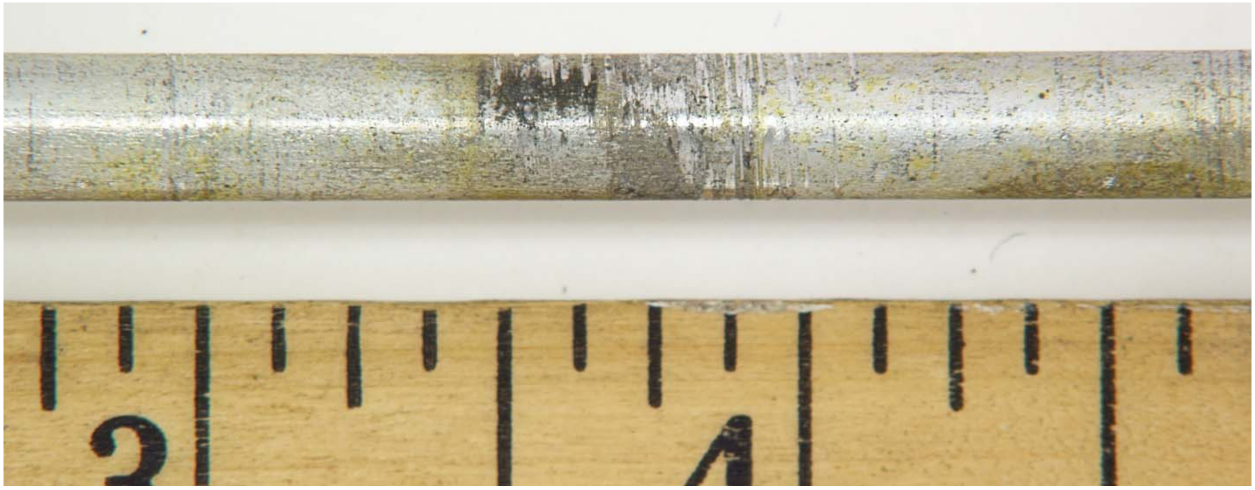

Figure 107. Mark on the Surface Formed by Contact Between the PRV Stem and the Spacer Guide from PRV 523.

Figure 108 and Figure 109 show PRV 696 and its discolored PRV stem, respectively. This PRV was a 250-psig set pressure PRV that was 57 years old. When the PRV stem was checked with a magnet, it was found to be non-magnetic. Subsequent EDS analysis of a piece from that PRV stem revealed that it was fabricated from a leaded brass, most likely CDA Alloy C36000, free-cutting brass. The high STD behavior of this PRV may have been related to contact of the brass stem with the brass spacer guide and the oxidation that occurred between those contacting surfaces. Similar composition materials in intimate contact under static loads tend to bond over time.

Figure 108. PRV 696, 250-psig Set Pressure PRV that Exhibited High STD Behavior.
This PRV was 57 years old.

Figure 109. PRV Stem from PRV 696.
Note the discoloration of the entire surface of the PRV stem. The tilt of the gasket holder resulted from bending while trying to remove the valve stem. EDS analyses revealed that this PRV stem was fabricated from brass.

Because some of the PRV stems that were checked with a magnet were magnetic and others were not, it was decided to check all PRVs undergoing forensic analysis with a magnet. Their responses are summarized in Table 6. As is shown in the table, 13 of the 250-psig set pressure PRVs and five of the 275-psig set pressure PRVs were non-magnetic. The remainder of the PRV stems were magnetic. EDS analyses were conducted on three of the non-magnetic PRV stems and three of the magnetic PRV stems to obtain a semi-quantitative analysis of the materials in those PRV stems. The results of these analyses are provided in Table 7. The results of the EDS analyses revealed that the non-magnetic PRV stems were produced from either 200 series or 300 series stainless steels or brass. The magnetic PRV stems were produced from either carbon or low alloy steels.

Although the other non-magnetic PRV stems were not analyzed using EDS, it is likely that they were austenitic stainless steel because of their color (silver) and general lack of corrosion. The other magnetic PRV stems most likely were carbon or low alloy steel.

The behaviors of the PRVs during pressure testing are listed in Table 6. Those results show that 16 of the 18 PRVs that exhibited high STD pressures had non-magnetic PRV valve stems. Those PRV valve stems generally would be considered corrosion resistant materials and, as was shown previously, those PRVs did not exhibit significant corrosion but they did exhibit the contact marks between the brass guide fittings and the PRV valve stems. The two PRVs that did not open had magnetic carbon or low alloy steel PRV valve stems. Three other PRVs with magnetic PRV valve stems exhibited high STD start-to-discharge behavior. Thus, whether the PRVs had corrosion resistant material PRV valve stems did not guarantee normal discharge behavior during pressure testing.

Table 6. Magnetic Response of the PRV Stems from PRVs Selected for Forensic Analysis

PRV ID	PRV Manufacturer	Stem Magnetic Response Performance Issue
250-psig Set Pressure		
96	A	Non-magnetic; HSTD
116	A	Non-magnetic; HSTD
140	A	Non-magnetic; HSTD
174	A	Non-magnetic; HSTD

PRV ID	PRV Manufacturer	Stem Magnetic Response Performance Issue
187	A	Non-magnetic; LSTD, leaked continuously
395	A	Non-magnetic; HSTD
455	A	Non-magnetic; HSTD
511	A	Non-magnetic; HSTD
559	G	Magnetic; LSTD
644	E	Magnetic; HSTD
660	A	Magnetic; HSTD
674	F	Magnetic; HSTD
696	D	Non-magnetic (brass) ; HSTD
699	D	Non-magnetic; HSTD
750	A	Non-magnetic; HSTD
771	A	Non-magnetic; HSTD
780	A	Non-magnetic
275-psig Set Pressure		
122	C	Magnetic; DNO
523	A	Non-magnetic; HSTD
593	A	Non-magnetic; HSTD
597	C	Magnetic; LSTD
650	A	Non-magnetic; HSTD
733	D	Non-magnetic; HSTD
760	C	Magnetic; DNO

Table 7. Results of EDS Analysis for PRV Stem Materials of Construction

PRV ID	MAGNETIC?	MOST LIKELY MATERIAL BASED ON EDS ANALYSIS
644	Yes	Low alloy steel coated with cadmium
597	Yes	Carbon steel coated with cadmium
559	Yes	Carbon steel coated with cadmium with a high sulfur content
96	No	Austenitic stainless steel; 300 series
116	No	Austenitic stainless steel; 200 series
696	No	Leaded brass; probably C36000

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

There were four PRVs that exhibited low STD pressure behavior. Those PRVs were PRVs 187, 559, 597, and 733. PRV 187 and PRV 559 had 250-psig set pressures and PRV 597 and PRV 733 had 275-psig set pressures. PRV 187 and PRV 559 leaked during pressure testing. PRV 187 never reached its set pressure whereas PRV 559 discharged at 245.2 psig, 98 percent of the minimum set pressure value. The reasons for the behavior of PRV 559 were described in Section 5.2 Seat Disc (Gasket) Material Analyses (leak at the small ring gasket used as the seal between the head of the stem and the gasket holder). In addition, the condition of the gasket from PRV 187 was discussed in Section 5.2.

PRV 187 was extremely rusty when it was received at Battelle. Figure 110 shows the rust deposits on the surfaces of the PRV that were exposed to the propane environment inside the tank. The surfaces of the spacer (rolled steel) were corroded and the surfaces of the set pressure locking nut were corroded (attacked by a corrosive environment). Most of the rust on the surface of the PRV stem, the spring, and the spacer inside the spring appeared to have been deposited on those surfaces rather than formed by corrosion of the surfaces. Similarly, the rust on the internal surface of the housing and the surface of the gasket holder shown in Figure 111 were deposited on those surfaces because the components were brass and would not have formed red rust when corroded. It was as if this PRV was exposed to rusty water after removal from the tank.

Figure 110. PRV 187.
Note the rust on the spacer, the spring, the lock nut, and the PRV stem. This PRV was 45 years old.

Figure 111. Discoloration of the Surfaces of the Brass Housing and the Gasket Holder from PRV 187.
Note the rust deposits on the internal surface of the housing and the gasket holder.

Figure 112, Figure 113, and Figure 114 show the rust coating on the surface of the PRV stem and on the surfaces of the gasket and the gasket washer. However, there did not appear to be a continuous path of rust across the sealing surface of the gasket. Consequently, there is no conclusive evidence to indicate why this PRV leaked around the gasket during testing.

Figure 112. PRV Stem from PRV 187.
Note the rust colored deposits on the surface to the left of the gasket holder and the black deposits to the left of the rust colored deposits.

Figure 113. Rust Deposits on the Surface Region of the Gasket that was Exposed to a Propane Environment During Service.

Figure 114. Rust Deposits on the Surface of the Gasket and the Gasket Washer that were Exposed to a Propane Environment During Service and Rust Particles on the Seal Region Surface.
Note the radial cracks in the outer circumferential ring of the gasket.

Figure 115 shows the appearance of PRV 597, a 275-psig set pressure PRV that exhibited low STD pressure behavior. This PRV was 40 years old but showed little evidence of corrosion during service (see Figure 116). The surfaces of the housing were discolored from exposure to the atmosphere and paint was present on the internal and external surfaces of the housing. Figure 117 and Figure 118 show the gasket from PRV 597. It appeared to be in relatively good condition; however, as shown in Figure 118 there was a replica of a dent in the machined surface of the housing in the surface of the gasket. The dent in the machined surface of the housing is shown in Figure 119. Those features in the gasket and the seal surface of the housing were the only deficiencies observed and they do not appear to be the reason for the low STD pressure behavior. As is shown in Figure 120 and Figure 121, the PRV stem from this PRV was somewhat corroded/discolored but it did not show a significant mark from contact with the brass spacer guide. Based upon this examination there is no conclusive evidence for the low STD pressure behavior.

Figure 115. PRV 597, 275-psig Set Pressure PRV that Exhibited Low STD Behavior.
This PRV was 40 years old.

Figure 116. Discoloration and Paint on the Internal and External Surfaces of the Housing from PRV 597.

Figure 117. Gasket from PRV 597.

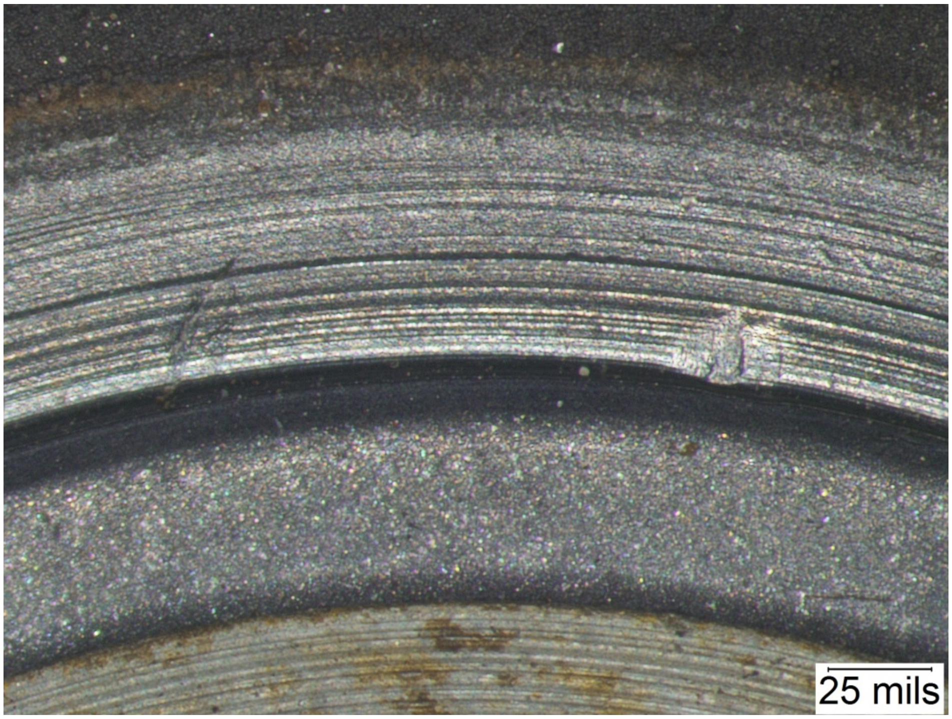

Figure 118. Replica of a Dent in the Machined Sealing Surface of the Housing on the Surface of the Sealing Region of the Gasket from PRV 597.

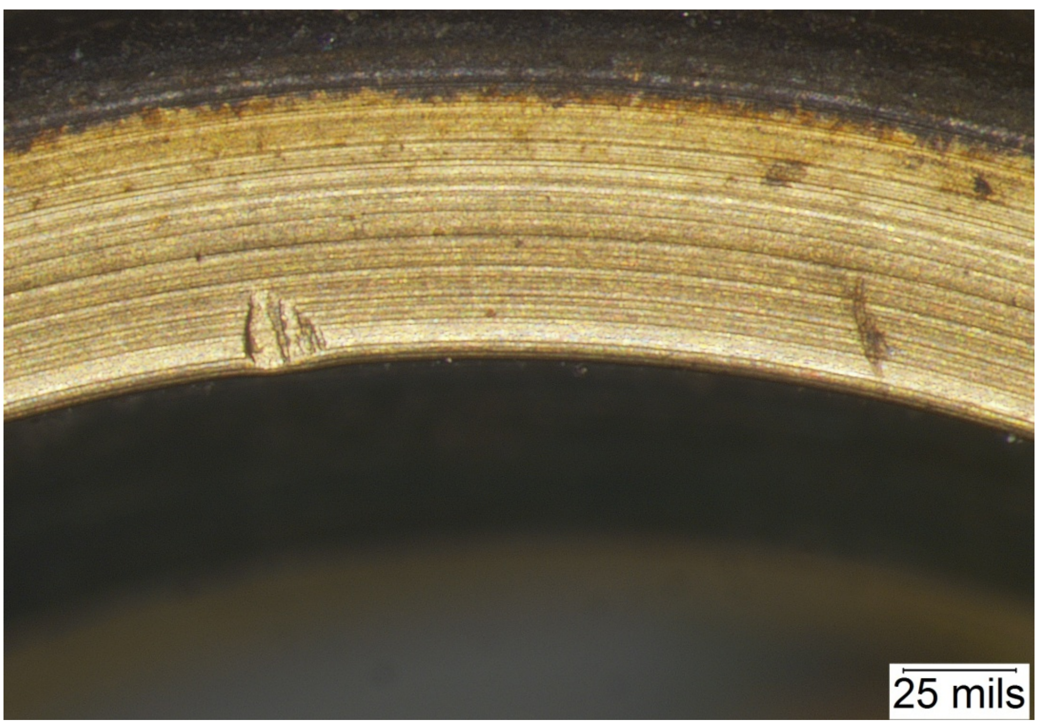

Figure 119. Dent in the Machined Sealing Surface of the Housing from PRV 597.

Figure 120. Somewhat Corroded PRV Stem from PRV 597.

Figure 121. Higher Magnification View of the Surface of the PRV Stem from PRV 597.

Figure 122 shows the appearance of PRV 733, a 275-psig set pressure PRV that also exhibited low STD pressure behavior. This PRV was 50 years old, but as is shown in Figure 123, the PRV appeared to be in relatively good condition. The spacer was discolored and some of the coating had chipped off the spring but there was no significant corrosion. As is shown in Figure 123, the surfaces on the brass housing were discolored from exposure to the atmosphere and there was some paint on the internal and external surfaces of the housing.

Figure 122. PRV 733, 275-psig Set Pressure PRV that Exhibited Low STD Behavior.
This PRV was 50 years old.

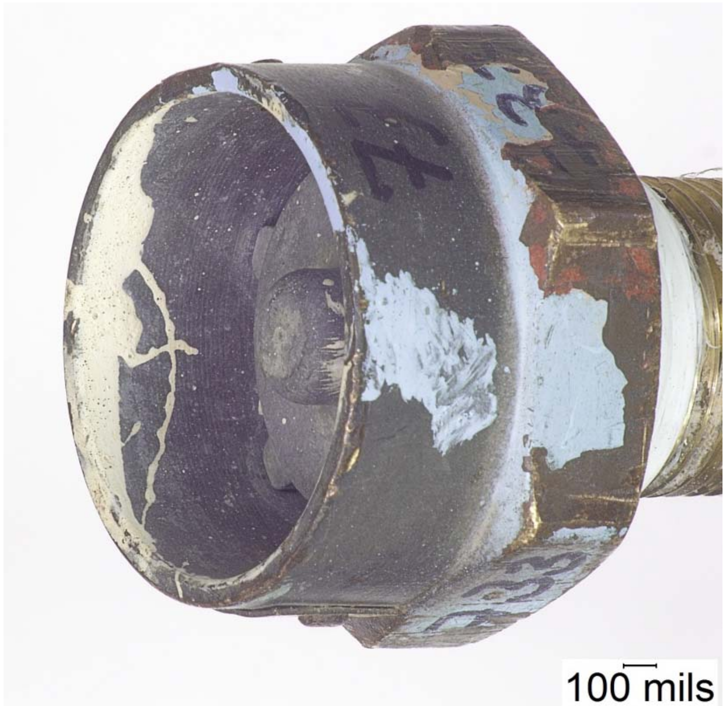

Figure 123. Discoloration and Paint on the Internal and External Surfaces of the Housing from PRV 733.

Figure 124 shows a crack in the sealing surface of the gasket from PRV 733. No other cracks were present in the gasket. It is possible that this crack caused the low STD pressure behavior of this PRV; however, when the gasket was removed from the holder for further examination, it broke into several pieces. Thus, it could not be confirmed whether the crack penetrated the gasket. Also, the average hardness of the gasket was 62.8 Shore D, the second highest hardness measured on the gaskets.

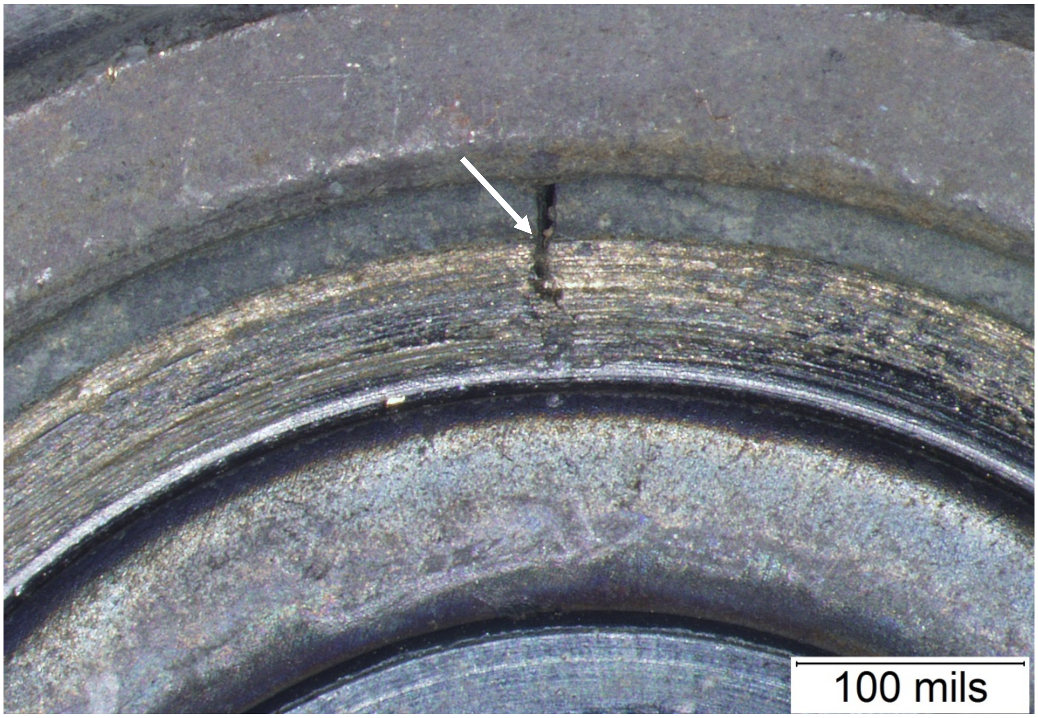

Figure 124. Crack in the Seal region Surface of the Gasket from PRV 733.

Figure 125 and Figure 126 show the contact marks and discoloration on the surface of the PRV stem. These marks did not contribute to the low STD pressure of the PRV.

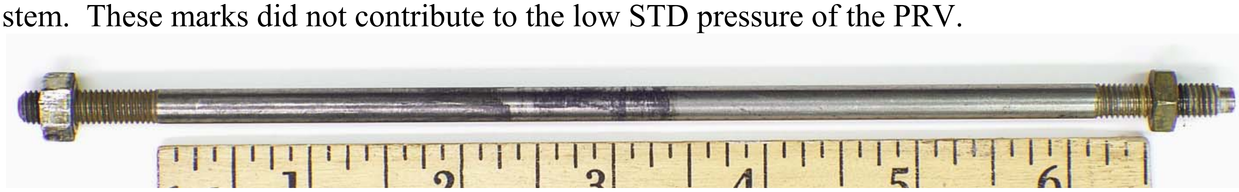

Figure 125. PRV Stem from PRV 733.

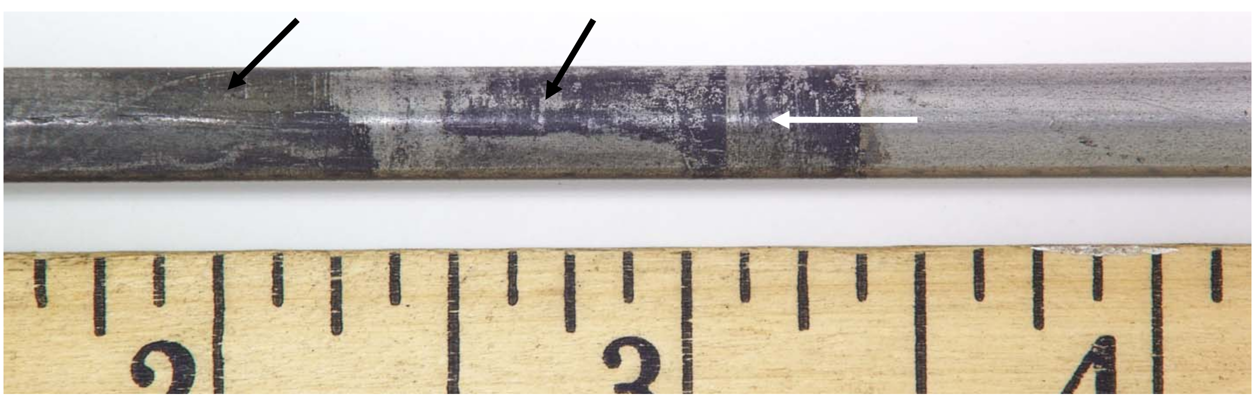

Figure 126. Mark (white arrow) on the PRV Stem from Contact with the Guide Washer and Dark Deposits (arrows) in the Surface Region that was Under the Spring.

Table 8. Summary of Detailed Examinations of PRVs

PRV ID	PRV AGE (yrs)	REASONS FOR DEMONSTRATED BEHAVIOR
PRV Did Not Open by 375 psig		
122	**34**	PRV stem stuck in the spacer guide
760	**39**	PRV stem stuck in the spacer guide
PRV Exhibited High STD Pressure		
96	**4**	Not conclusive, possibly PRV stem stuck in guide washer
116	**16**	Not conclusive, possibly PRV stem stuck in guide washer
395	**31**	Not conclusive, possibly PRV stem stuck in guide washer
523	**31**	Not conclusive, possibly PRV stem stuck in guide washer
644	**53**	Not conclusive, possibly PRV stem stuck in guide washer
674	**53**	Corrosion of the PRV stem and spacer guide
696	**57**	Not conclusive, possibly sticking of brass stem to the brass spacer guide
750	**27**	Not conclusive, possibly PRV stem stuck in guide washer
PRV Exhibited Low STD Pressure		
187	**45**	Not conclusive, PRV leaked around gasket
559	**45**	PRV leaked and finally discharged through a ring gasket between the PRV stem and the gasket holder
597	**40**	Not conclusive
733	**50**	Possibly a crack through the seal region of the gasket

6.0 Summary and Conclusions

6.1 Summary

The objective of this experimental test program of PRVs was to attempt to provide data to evaluate 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 200 PRVs removed from service, varying in age from less than 1 year to more than 50 years. The PRVs were tested to a test protocol that was developed to mimic real world conditions. The test protocol included conditioning the PRV in a propane environment, testing the PRV at a temperature representative of a hot day, and increasing the pressure to the PRV at a much slower rate (similar to a tank subjected to ambient heating).

This study found that:

1. All but two PRVs tested opened within the maximum test pressure of 375 psig (1.5x a propane tank with 250-psig working pressure, equivalent to the hydrotest pressure). Both PRVs that did not open were 275-psig set pressure, over 30 years old, and identical PRVs from the same manufacturer.

2. A total of 102 PRVs had STD pressures within the NPC. These PRVs ranged in age from new to over 50 years old.
3. Beyond 15 to 20 years of age, there is a greater tendency for inconsistent PRV performance against the NPC. STD pressures ranged from 50 psig below the set pressure to 100 psig above the maximum set pressure (275 psig for 250-psig set pressure PRVs).
4. Statistically significant differences were noted for some manufacturers and some PRV sizes. The root cause could be age related differences in PRV groupings or an inherent design difference that affects the PRV performance under the test protocol.

6.1.1 Visual Inspections

All new PRVs were documented as 'good' condition for their visual inspection. The percentage of PRVs in 'good' condition slowly declines as the age of the PRV increases coincident with the rise of PRVs that received a 'marginal' rating for the visual inspection. The first 'poor' visual inspection ratings appear after 10 years of service. At ages in excess of 20 years the majority of PRVs receive a 'marginal' rating. Note that these ratings are an indication of the PRV condition based on observations of care and maintenance; they are not measures of actual PRV performance.

Manufacturers A, B, and C all had similar percentages of good, marginal, and poor ratings. The lack of good or poor ratings for Manufacturers D, E, F, and G are likely due to the relatively low number of PRVs in these categories (20 combined) rather than an inherently superior design, manufacturing process, or maintenance. The overall percentages of PRVs receiving good, marginal, and poor visual ratings did not have a strong correlation to connection size or set pressures.

The test results show broad scatter in PRV performance against the NPC for PRVs older than 15 years of age for 250-psig set pressure PRVs and 30 years of age for 275-psig set pressure PRVs. The results also show that there are a higher percentage of PRVs older than 15 years receiving a 'marginal' or 'poor' visual inspection rating. Although high STD pressures begin to appear after 10 years, there does not appear to be a discernible trend of their percentage increasing with age until after 25 to 30 years of age (see Figure 3). The data suggests that PRV performance may be influenced by PRV maintenance – PRVs that received 'marginal' or 'poor' visual inspection ratings tend to have STD pressures outside the bounds of the NPC.

6.1.2 PRVs that Did Not Open

Only two out of 200 PRVs tested (1percent of the test population) did not open after reaching 375 psig. Both of these PRVs (PRV 122 and PRV 760) had 275-psi set pressures and the fact that they did not open was not found to be statistically significant (could have occurred by chance). Both PRVs were produced by Manufacturer C and are identical models. PRV 122 was 34 years old and PRV 760 was 39 years old. Examinations of these two PRVs showed many similar features, including stems that were difficult to remove from the PRV housing and severely corroded gasket holders. Based upon the examination of PRV 122 and PRV 760, the Battelle investigators believe that the reason for the observed behavior was that the PRV stems had become 'stuck' to the relatively long (2-inches) brass spacer guides during service even though significant corrosion did not occur between those surfaces.

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

As shown in Figure 43, the probability for a PRV to discharge above 110 percent of the set pressure ranged from approximately 17 to 26 percent (with 95-percent confidence) for new PRVs to 52 to 62 percent (with 95-percent confidence) for 40 year old PRVs.

PRVs that discharged late (>120 percent of the set pressure) were also considered to have performance outside the bounds of the NPC. As shown in Figure 3, the probability for a PRV to discharge above this limit accelerates for PRVs older than 25 to 30 years of age. The probability for new PRVs to open 120 percent above the set pressure can range from approximately 8 to 15 percent (with 95-percent confidence) increasing to 31 to 42 percent (with 95-percent confidence) for 40 year old PRVs.

Of the PRVs selected for forensic analysis, fifteen of the 250-psig set pressure PRVs and three of the 275-psig set pressure PRVs exhibited high STD pressures against the NPC. All of these PRVs were examined visually and disassembled for more detailed examinations to determine to the extent possible the most probable cause for the high STD pressure behavior.

Examination of those PRVs revealed that most of them showed relatively little evidence of deterioration as a result of their service lives. The one high STD PRV that exhibited the most extensive corrosion on its exposed components was PRV 674, which had been in service for 53 years. This PRV was tested twice to 350 psig without opening; on the third pressurization cycle the PRV opened at 254 psig, very near the set pressure for the PRV. When the PRV was disassembled, the stem was stuck in the spacer guide and PRV housing. The stem was pushed out of the housing and spacer guide using an Instron Universal Testing machine. The load required to get measurable movement of the stem was 968.2 pounds (displacement was 0.015-inches). The load then dropped to between 500 and 600 pounds to move the stem. Based upon those measurements, it is difficult to understand how the PRV discharged at 254 psig during the third pressurization cycle. The Battelle investigators concluded that the high STD behavior of PRV 674 was caused by the corrosion of the stem and spacer fitting that was exposed to the environment inside the propane tank. This type of corrosion indicates that there was a significant amount of moisture inside the tank.

None of the other PRVs that exhibited high STD behavior during testing exhibited the extent of corrosion to their components as did PRV 674. However, all of them did exhibit a distinct mark on the PRV stem formed by contact between the PRV stem and the spacer guides. In addition, none of the PRVs exhibited evidence of sticking of the gaskets when they were disassembled. Consequently, the Battelle investigators conclude that the most likely reason for their high STD behavior was the sticking of the PRV stem to the spacer guide or guide washers.

When non-lubricated metallic materials are in intimate contact under essentially static loads, they will stick together because of slight oxidation of the surfaces even though significant corrosion does not occur. This behavior suggests that the use of solid film lubricants or CPCs (corrosion prevention compounds) on the surface of the PRV stems and/or the guide spacers might be highly beneficial to improve PRV performance. In addition, appropriate polymer bushings or guides between those components may prevent sticking.

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

Of the PRVs selected for forensic analysis, there were four PRVs that exhibited low STD pressure behavior. Those PRVs were PRVs 187, 559, 597, and 733. PRV 187 and PRV 559 leaked during pressure testing. PRV 187 never reached its set pressure whereas PRV 559 discharged at 245.2 psig, 98 percent of the minimum set pressure value. PRV 559 leaked at the small ring gasket used as the seal between the head of the stem and the gasket holder.

The internal components of PRV 187 were extremely rusty. Most of the rust on the surface of the PRV stem, the spring, the spacer inside the spring, the housing, and the gasket holder appeared to have been deposited on those surfaces rather than formed by corrosion of the surfaces. It was as if this PRV was exposed to rusty water after removal from the tank. However, there did not appear to be a continuous path of rust across the sealing surface of the gasket. Consequently, there is no conclusive evidence to indicate why this PRV leaked around the gasket during testing.

PRV 597 appeared to be in relatively good condition; however, there was a dent in the machined surface of the housing that also imprinted on the gasket. These features were the only deficiencies observed and they do not appear to be the reason for the low STD pressure behavior. Based upon this examination there is no conclusive evidence for the low STD pressure behavior.

PRV 733 also appeared to be in relatively good condition. The spacer was discolored and some of the coating had chipped off the spring but there was no significant corrosion. PRV 733 did have a crack in the sealing surface of the gasket. It is possible that this crack caused the low STD pressure behavior of this PRV. Also, the average hardness of the gasket was 63 Shore D, the second highest hardness measured on the gaskets.

6.2 Conclusions

All tested 250-psig set pressure PRVs opened by 150 percent of the working pressure (375 psig). Only two 275-psig set pressure PRVs did not open by 375-psig[9] and it is believed that the observed behavior was due to the PRV stems becoming ‘stuck’ to the spacer guides during service even though significant corrosion did not occur between those surfaces.

For PRVs that did open, the STD pressure exhibited a high amount of variability. A considerable population did not open within the NPC of 100 percent to 120 percent of the set pressure (98 PRVs). Small differences were observed based on various breakdowns including size, manufacturer, and age but none of the breakdowns distinguished themselves as particularly good or bad. The most likely reason for their high STD behavior was the sticking of the PRV stem to the spacer guides or guide washers except for PRV 674 which showed extensive corrosion on several PRV components that likely caused the high STD.

[9] Note that the maximum test pressure of 375 psig is less than 150 percent of the PRV set pressure and it therefore is not conclusive that these PRVs would not have opened before the hydrotest pressure of tanks with a design working pressure of 275 psig on which they were installed.

Age still appears to be the single most significant factor affecting PRV performance. The forensic analyses indicated that sticking of the PRV stem to the guide spacers or guide washers was the most likely cause for the high STD pressures and PRVs not opening during testing. Additionally, the corrosion found on some of the internal components of the PRVs examined is suspected to have come from high moisture in the propane. Moreover, older PRVs are more susceptible to a build-up of dirt/debris within the PRV especially if the rain cap has been removed. This dirt/debris can plug the weep hole and allow water to collect in the PRV body. As such, PRV maintenance (checking rain caps and weep holes) may be just as important as the age of the PRV.

An additional factor is the knowledge that PRV manufacturers intentionally set higher PRV set pressure tolerances to meet both UL 132 and ASME Section VIII requirements. This was due to the California Title 8 requirement that only ASME rated PRVs could be used on ASME containers. Since California's adoption of the 1998 version of NPFA 58, UL PRVs can now be used without a California setting. Several of the California setting PRVs shows higher STD pressures. Nineteen of the 28 California setting PRVs had STD pressures over 275 psig (110 percent of 250 psig). Only 9 California setting PRVs had STD pressures over 312.5 psig (110 percent of 275 psig). The remaining California setting PRVs (9 of the 28) had STD pressures between 230 and 275 psig. These higher initial set pressure tolerances are likely contributing to the statistically significant higher STD pressures for older PRVs.

Based on the observed data, it is unlikely that testing a larger number of PRVs would affect the outcomes of this performance test program. While small shifts in the probability of a PRV opening may be realized, the data will likely still indicate that a majority of the PRVs will open by 150 percent of the tank working pressure with a substantial portion of that population having a STD pressure outside the NPC.

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Appendix A

Sample PRV Collection Letter

Battelle
The Business of Innovation

Month DD, 2011

Company
Attn: Contact
Street
City, State, ZIP
Country

Dear _____,

RE: PERC Project to Evaluate the Performance and Service Life of Pressure Relief Valves on Customer Propane Tanks

Thank you for your cooperation and participation in the PERC project to evaluate the performance and service life of pressure relief valves (PRVs) on customer propane tanks. To assist with this effort Battelle is collecting and testing functional residential ASME tank PRVs from various geographic locations around the U.S. that have been removed from service within the past month for reasons other than their malfunction. We are interested in all brands, models, and ages, both internal and external. We are hoping to receive valves as new as 1 year old to as old as several decades.

Before shipping the PRVs to Battelle, we would appreciate if you could fill out as much information as you can on the enclosed information tags for each PRV and include the tag with the PRV when complete. Please provide as much information as possible; however if some of the information is unknown we are still interested in receiving the PRV (provided that it was recently taken out of service). The tag provides packaging instructions, contact information, and Battelle's shipping address. Once the PRVs are ready to ship, please call our Administrative Assistant, Cheryl Weil, at (614) 424-3976 - she will arrange a FedEx pick-up so that the shipping costs can be billed to Battelle.

If you have any questions or concerns, do not hesitate to contact Stephanie Flamberg at (614) 424-3061. If you prefer email please send your questions to flamberes@battelle.org, respectively. Your participation in this project is greatly appreciated.

Sincerely,

Stephanie Flamberg
Principal Research Scientist
Battelle - Energy Systems & Carbon Management

Enclosures: PRV Information Tags and Packaging Bags

505 King Avenue Columbus, Ohio 43201-2693 800.201.2011 solutions@battelle.org www.battelle.org

Appendix B

Test Protocol Development

One of the issues identified after completion of the 2009 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 2009 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, tasks were conducted to better understand what the 'real world' conditions might look like. 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.

B.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.

B.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.

B.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 B-1. As can be seen from Table B-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 B-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

B.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[10]) was reviewed to identify elastomeric materials suitable for propane use and the recommended temperature limits of those materials. Table B-2 summarizes this information.

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 B-2. Thermal Limits of Elastomeric Seal Materials for Propane Applications

Material	Exposure Rating Grade[11]	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

B.3 Thermal Modeling of a Propane Tank

B.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

[10] http://www.applerubber.com/sdg/guide2/material_guide/src/compat.pdf
http://www.applerubber.com/sdg/guide2/material_guide/src/genprop.pdf
[11] This refers to the suitability of the material for use in propane service.

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.
    - 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.

B.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 B-1. The same curves are shown for a 1,000-gallon tank in Figure B-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.

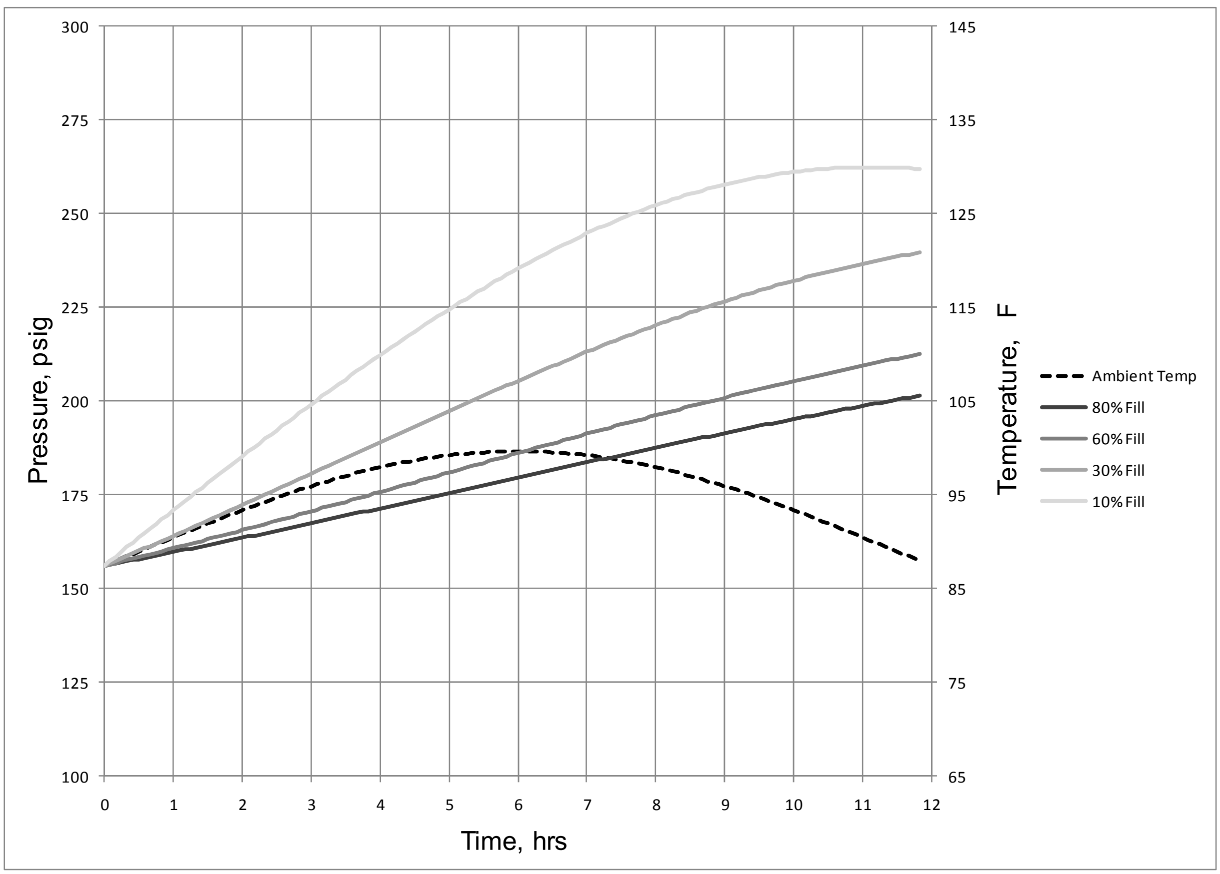

Figure B-1. Thermal Response of 500 Gallon Propane Tank

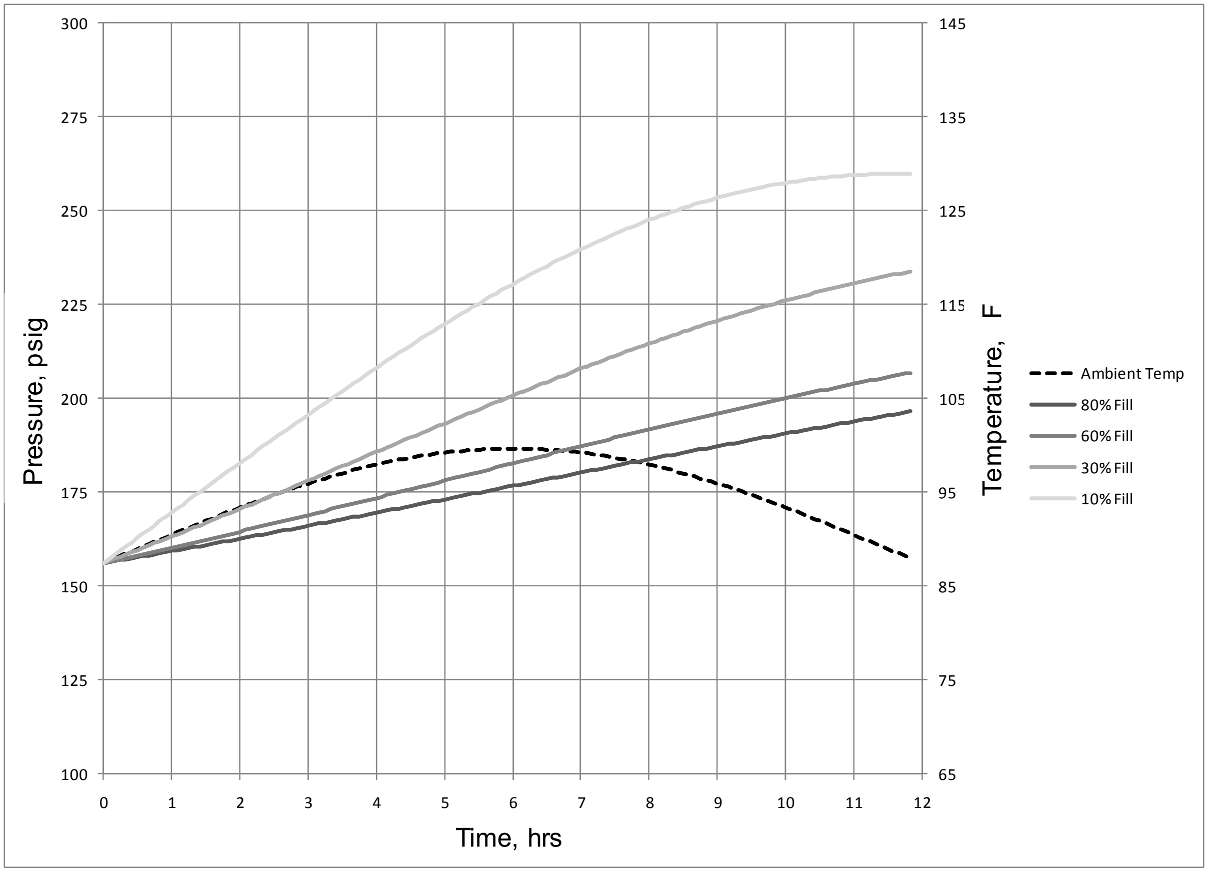

Figure B-2. Thermal Response of 1,000 Gallon Propane Tank

A summary of the modeled pressure rise rates is presented in Table B-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 B-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 B-1 and Figure B-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.