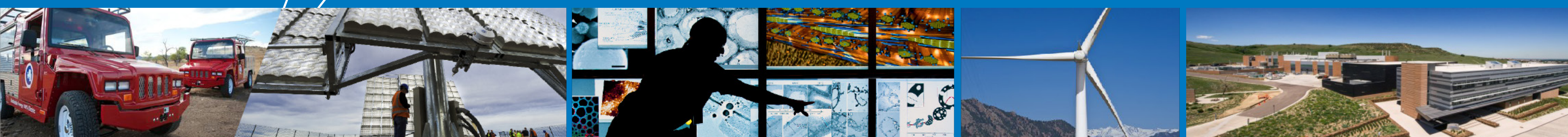
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Hydrogen Component R&D



2016 DOE Annual Merit Review
Hydrogen Safety Codes and Standards

Robert Burgess (PI), Matthew Post, Arlen Kostival, William Buttner, Carl Rivkin

National Renewable Energy Laboratory

June 07, 2016

Project ID # SCS002

Overview

TIMELINE

- Start date: 10/1/2015
- End date: 09/30/2016*

*Project continuation and direction determined annually by DOE

BARRIERS

Multiyear RD&D Barriers

- ***A.*** Safety data and information: Limited access and availability
- ***C.*** Safety is not always treated as a continuous process
- ***F.*** Enabling national and international markets requires consistent RCS
- ***G.*** Insufficient technical data to revise standards
- ***H.*** Insufficient synchronization of national codes and standards
- ***J.*** Limited participation of business in the code development process
- ***K.*** No consistent codification plan and process for synchronization of R&D and code development

BUDGET

- Funding for FY15: **$330K**
- Planned FY16 funding: **$75K**

PARTNERS

- Industry (component manufacturers, automotive original equipment manufacturers, station suppliers)
- Laboratories/universities (SNL, CDFA, PNNL, JRC-IET, NHTSA, NIST, others)
- Codes and standards development organizations (CGA, SAE, CSA, ASME, ISO, UL, NFPA, IEC, GTR, ANSI, others)

Relevance: PRD Lessons Learned

- **Pressure relief devices are a critical safety device that are required to protect storage cylinders and pressurized systems against burst failure**
- **PRD inadvertent release can create public concern due to hydrogen dispensers being located in public areas**
- **PRD venting of a flammable gas has inherent higher risk compared to venting of a non-flammable gas**

HYDROGEN **TOOLS**

LOG IN

WORKSPACES | RESOURCES | FORUMS | PARTNERS | ABOUT

Home » Lessons Learned » Pressure Relief Device Fails at Fueling Station

Pressure Relief Device Fails at Fueling Station

Severity:	Leak:	Ignition:
Incident	Yes	Yes
		IGNITION SOURCE: EITHER STATIC ELECTRICITY OR SPARK FROM ESCAPING PARTICLE

2012

A pressure relief device (PRD) valve failed on a high-pressure storage tube at a hydrogen fueling station, causing the release of approximately 300 kilograms of hydrogen gas. The gas ignited at the exit of the vent pipe and burned for 2-1/2 hours until technicians were permitted by the local fire department to enter the station and stop the flow of gas. During this incident the fire department evacuated nearby businesses and an elementary school, closed adjacent streets, and ordered a high school to shelter in place.

There were no injuries and very little property damage. The corrugated roof on an adjacent canopy over a fueling dispenser was slightly singed by the escaping hydrogen flame, causing less than $300 in damage.

Source: DOE/PNNL Hydrogen lessons learned database, https://h2tools.org/lessons

Hydrogen release from a failed PRD can result in large quantities of hydrogen discharge which creates risk, both by inadequate dispersion of the venting gas cloud and by potential for finding an ignition source

Relevance: Pressure Relief Device Reliability Limitations

- **Pressure relief devices are a critical safety device that are required to protect storage cylinders and pressurized systems against burst failure**
- **PRD's reliability has been a known concern within the industrial gas community. One PRD failure mode that is known to be an issue is premature or unintended release. The relative safety risk of this failure mode is dependent on the dispersion environment.**
  - Reliving to a vent stack in an industrial environment is a low level safety risk due to limited public exposure and operations safety controls .
  - Hydrogen relief to a vent stack at a retail dispensing station is a higher safety concern and a potential public exposure risk.
  - Relief of a transport cylinder can be a significantly higher risk depending on environmental conditions at the time of release (wind, temperature, accident scenarios, etc.). The potential to trap venting hydrogen gas could lead to a gas cloud explosion.
- **Hazard analysis should be used to determine if installing a PRD can increase the overall risk compared to the risk of no relief device on a cylinder**
- **CGA has performed transport cylinder bonfire testing to determine the failure modes and risks of engulfing fire scenarios**

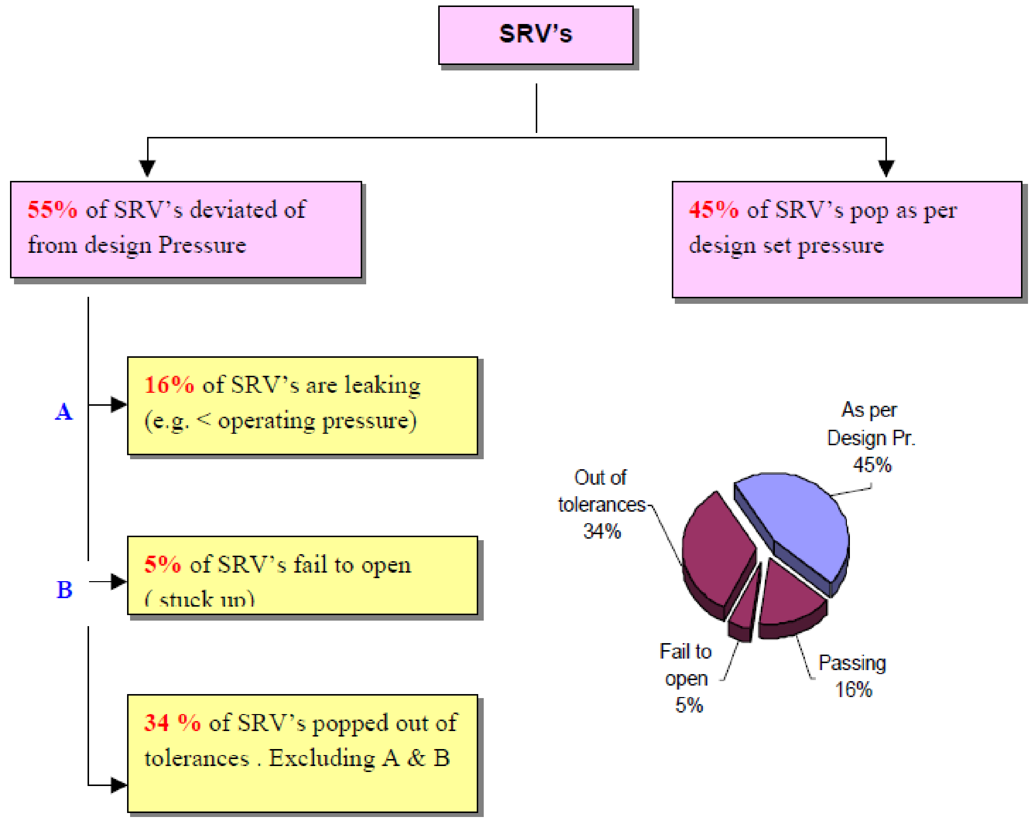
Relevance: Relief Valve Reliability

Industry study of in-service relief valves identifies significant reliability gap

- Industry study shown at right depicts results of plant wide study
- 100% of in-service relief valves were pulled from operation and inspected
- 55% of the relief valves were out of specification, either failed to open within ± 3% of the setpoint or leaked above specification

THE HIDDEN FACTS OF PROCESS SAFETY VALVE RELIABILITY

Mohammad M. Alkhaldi,
Saudi Arabian Fertilizer Company (SAFCO), Saudi Arabia



Reference: Alkhaldi, M., *The Hidden Facts of Process Safety Valve Reliability*, International Fertilizer Industry Technical Conference Proceedings, April 2004

Approach: Pressure Relief Device Task Objective

The objective of the pressure relief device project is to conduct research on pressure relief device failures with the goal of gaining an improved basic understanding of high pressure hydrogen operational safety and risk. Results are provided to manufacturers and system suppliers for enhanced design, operation and quality control of pressure relief devices for use on high pressure hydrogen systems. Tasks on this project include the following

- Reliability testing of pressure relief devices under elevated stresses and end of life conditions
- Collection of operational data from failed pressure relief devices in actual service
- Survey of pressure relief device reliability from information supplied by industry, early market experience and published literature
- Dissemination of results through outreach and collaboration

Approach: Performance Based Testing Methodology

- **SAE J2579 diagram shows the relationship between operating demand and system capability (failure)**
- **Desire for failure data to show low sigma (predictable end of life)**
- **NREL is testing two valves that have known field failure. Pressure relief device 440C nozzle field failure occurred after three months operation.**
- **Response distribution for performance based testing methodology should be able to reproduce failure with repeatable results and low sigma distribution**

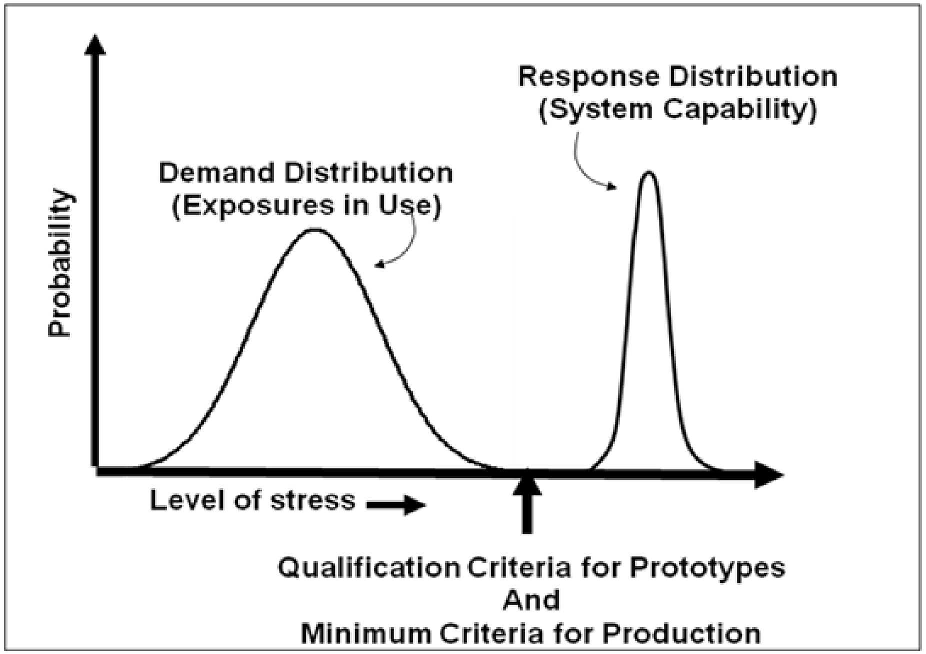


FIGURE 3 - RELATIONSHIP OF DEMAND AND CAPABILITY DISTRIBUTIONS

Source: SAE J2579 “Standard for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles”

Accomplishments and Progress:
Reliability Curve (Statistical Distribution)

Typical reliability curves for well behaved data will result in failures occurring within a well defined time (normal distribution)

- **Reliability data with a normal distribution typically has a well understood failure mechanism (material degradation, fatigue, aging etc.)**
- **PRD reliability data has not been shown to exhibit a normal distribution**

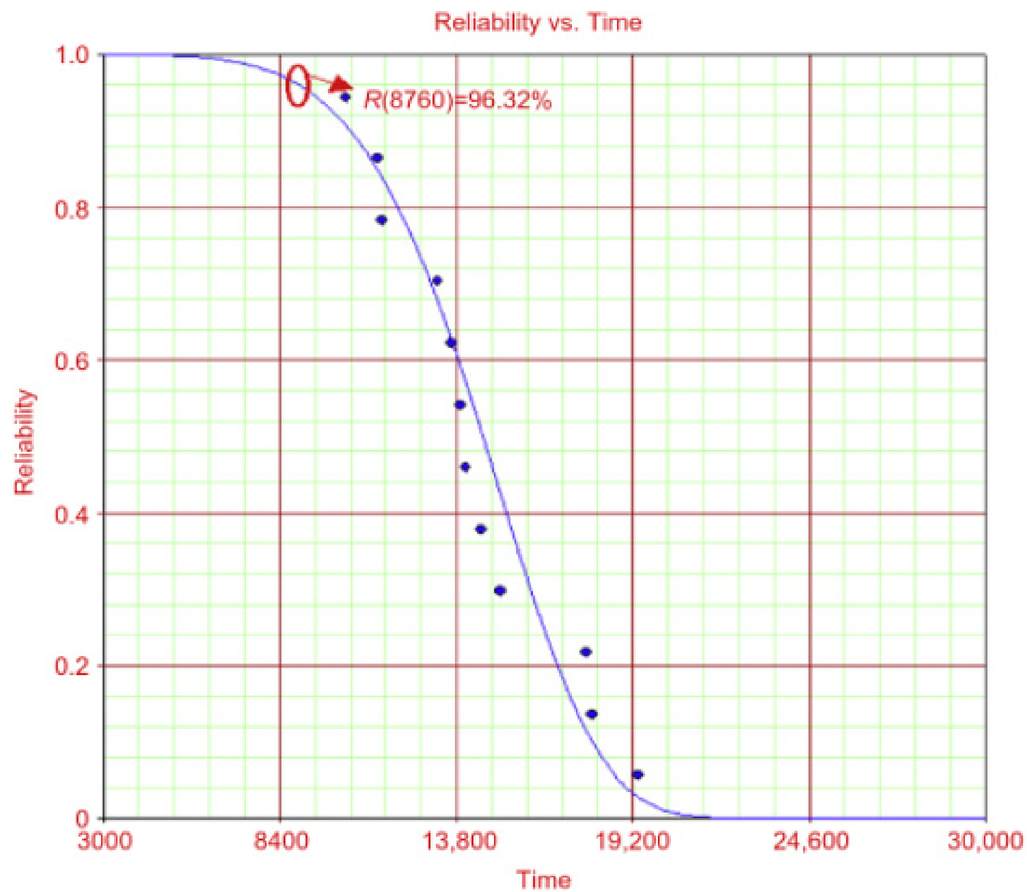
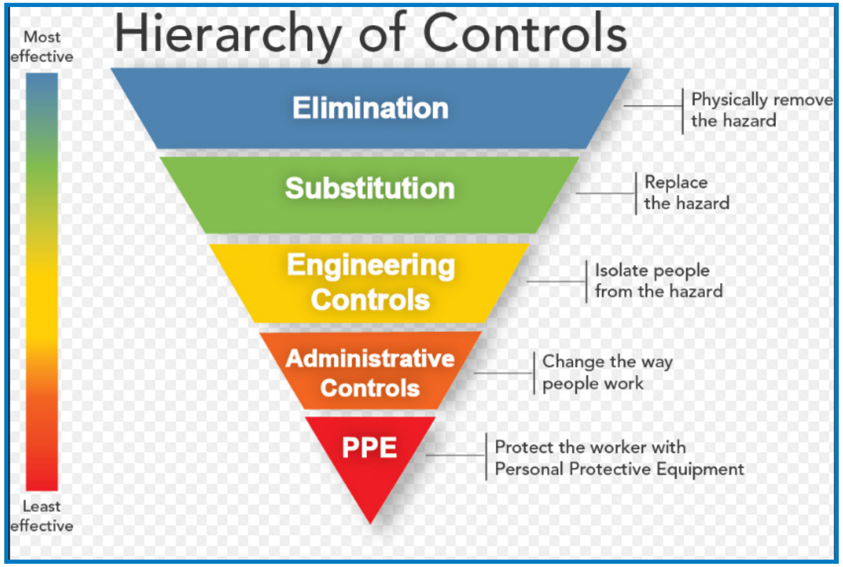


FIGURE 2-7 Logic element reliability curve under operational conditions.

Reference: "Gas and Oil Reliability Engineering", 2013

Accomplishments and Progress: Hierarchy of Safety Controls

- **A gap exists between expected relief valve reliability and field experience**
  - Relief valves are known to fail unexpectedly
  - Eliminating relief valve failures will require a better fundamental understanding of failure mechanisms
  - Valve failure modes, where hydrogen is released up vent stack, is not a major safety issue at an industrial site but could result in significant public risk at hydrogen fueling stations
- **Status of hydrogen relief valve hierarchy:**
  - **Elimination:** Future work required to understand failure root causes and support R&D for better product reliability
  - **Substitution:** Removal of relief valves is (example: CGA recommendation to remove relief valve requirements from PHMSA Code)
  - **Engineering and Administrative Controls:** Typical manufacturer recommendation is three year maintenance cycle (reset and repair)
  - **PPE:** Often required in industrial gas environment but not practical for retail sales of hydrogen



Relief valve reliability is often dependent on Engineering and Administrative Controls which can be effective with proper adherence to safety best practices but a design fix is a better solution to eliminate risk

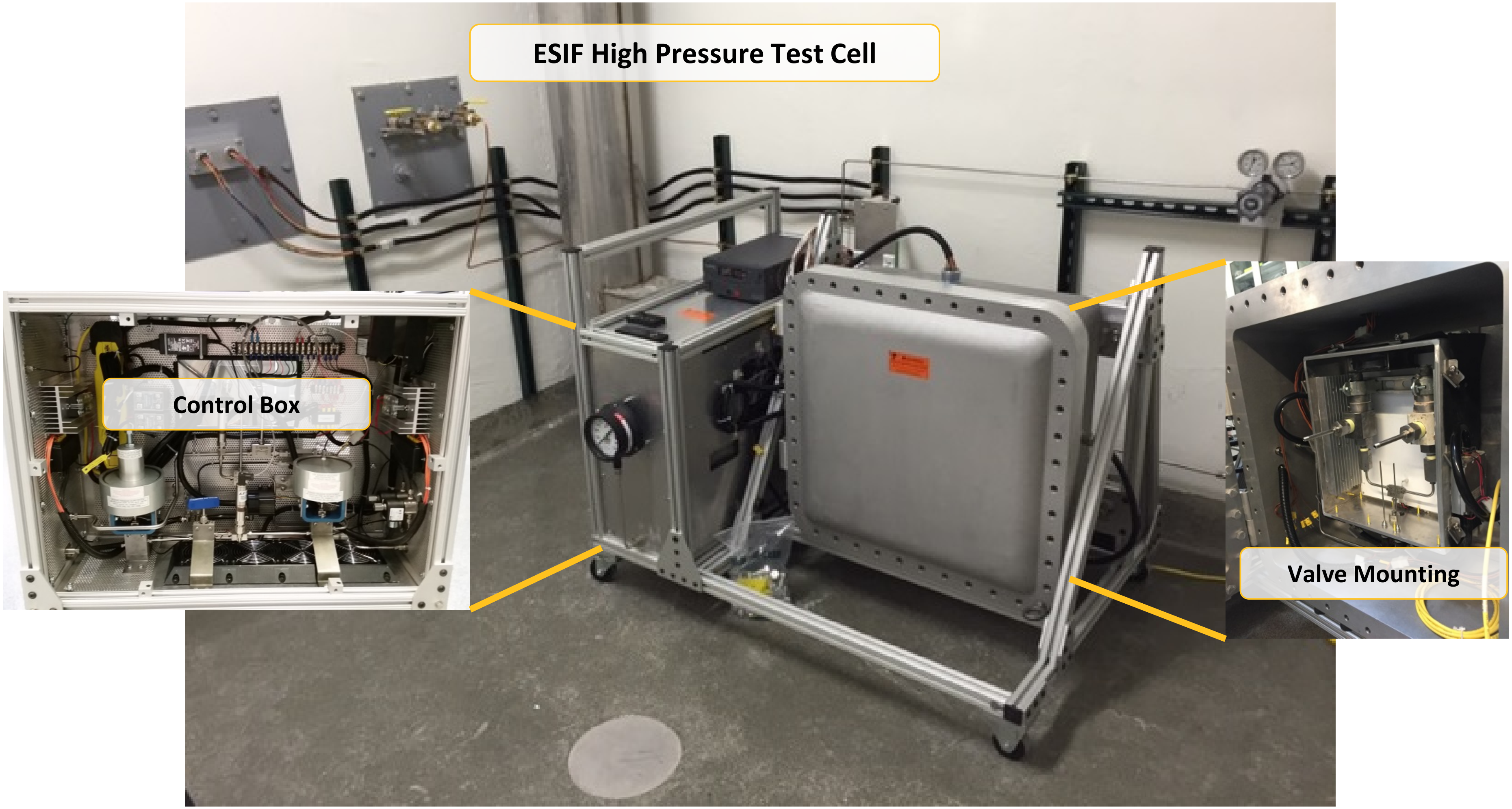
Accomplishments and Progress: Relief Valve Testing

- **Qualitative ALT (Accelerated Life Testing) testing to duplicate known field failure under controlled laboratory conditions**
- **Accelerated stresses of temperature and pressure in hydrogen environment**
- **Leak detection to identify point of failure**

Relief valve apparatus
installed in ESIF high pressure test bay

Relief valve programmable logic controller
(PLC) control box

Accomplishments and Progress: Test Device Installation

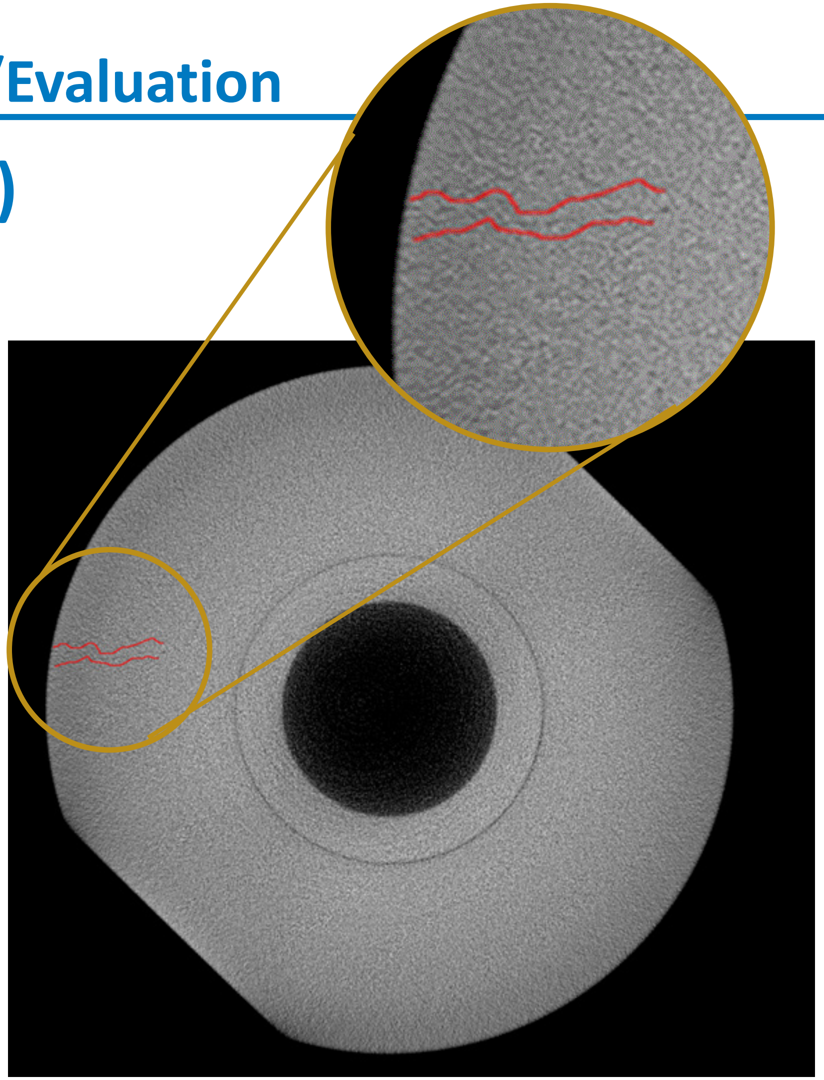


ESIF high pressure test cell allows for safe operation of hydrogen systems, designed for end of life component testing

Accomplishments and Progress: Nozzle Non-Destructive Inspection/Evaluation

Computed Tomography (CT Scan)

- X-Ray technique capable of detecting subsurface flaws and inclusions
- Top view images taken at intervals of .02 mm, defect is visible over ten image slices (defect size ~ 0.2 mm long x 6.2 mm deep)
- Defect is detected on 440C relief valve nozzle S/N 586381 after three-year operation in hydrogen service at NREL's Wind-to-Hydrogen demonstration facility
- Two pressure relief valves were selected for testing, one with known crack and one free from preexisting condition
- Post test CT Scan is being conducted to determine overall crack growth rate and inspect for further crack initiation

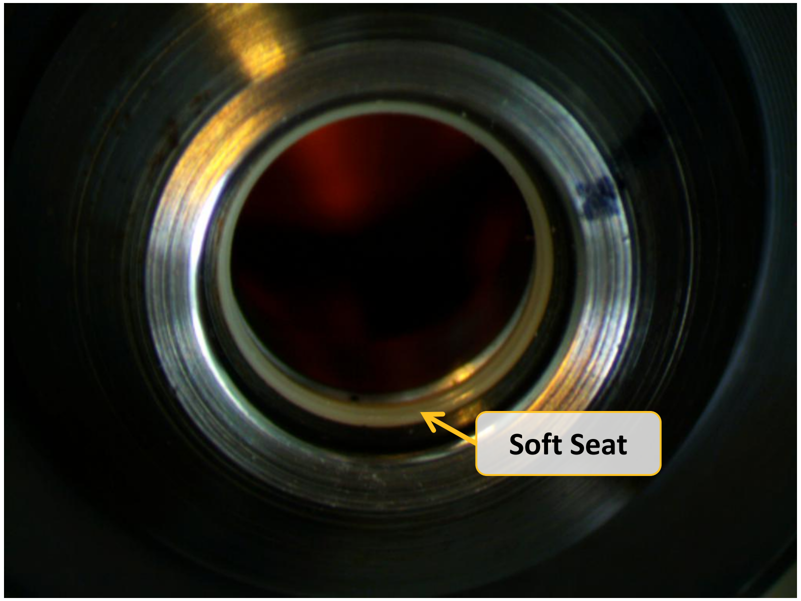


S/N 586381, slice 98, 8.5659 mm (Nikon Metrology Inc.)

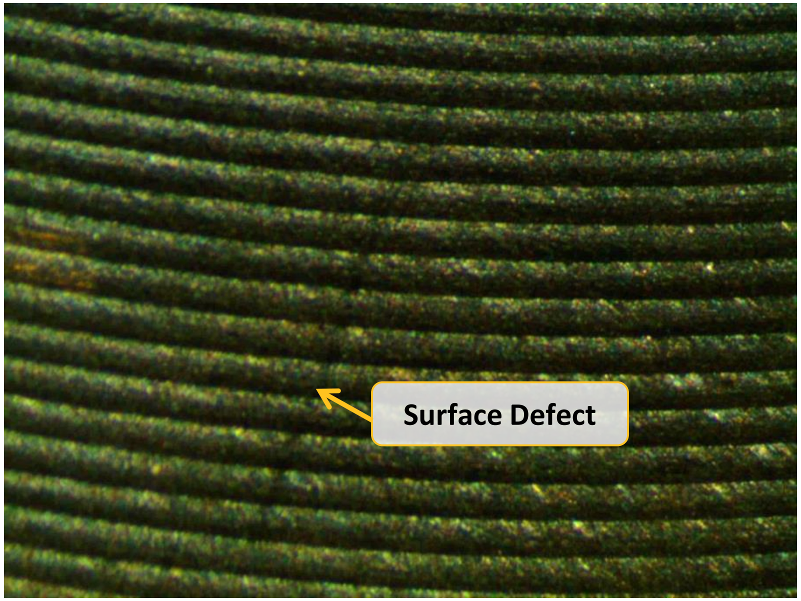
Result: Defect size did not result in sufficient stress concentration to accelerate crack growth to failure over 10 years equivalent accelerated life test.

Accomplishments and Progress: Relief Valve Nozzle Inspection

- Relief valve has been in service for three years and shows evidence of operational and/or installation wear
- Documented condition of nozzle at start of accelerated life cycle testing

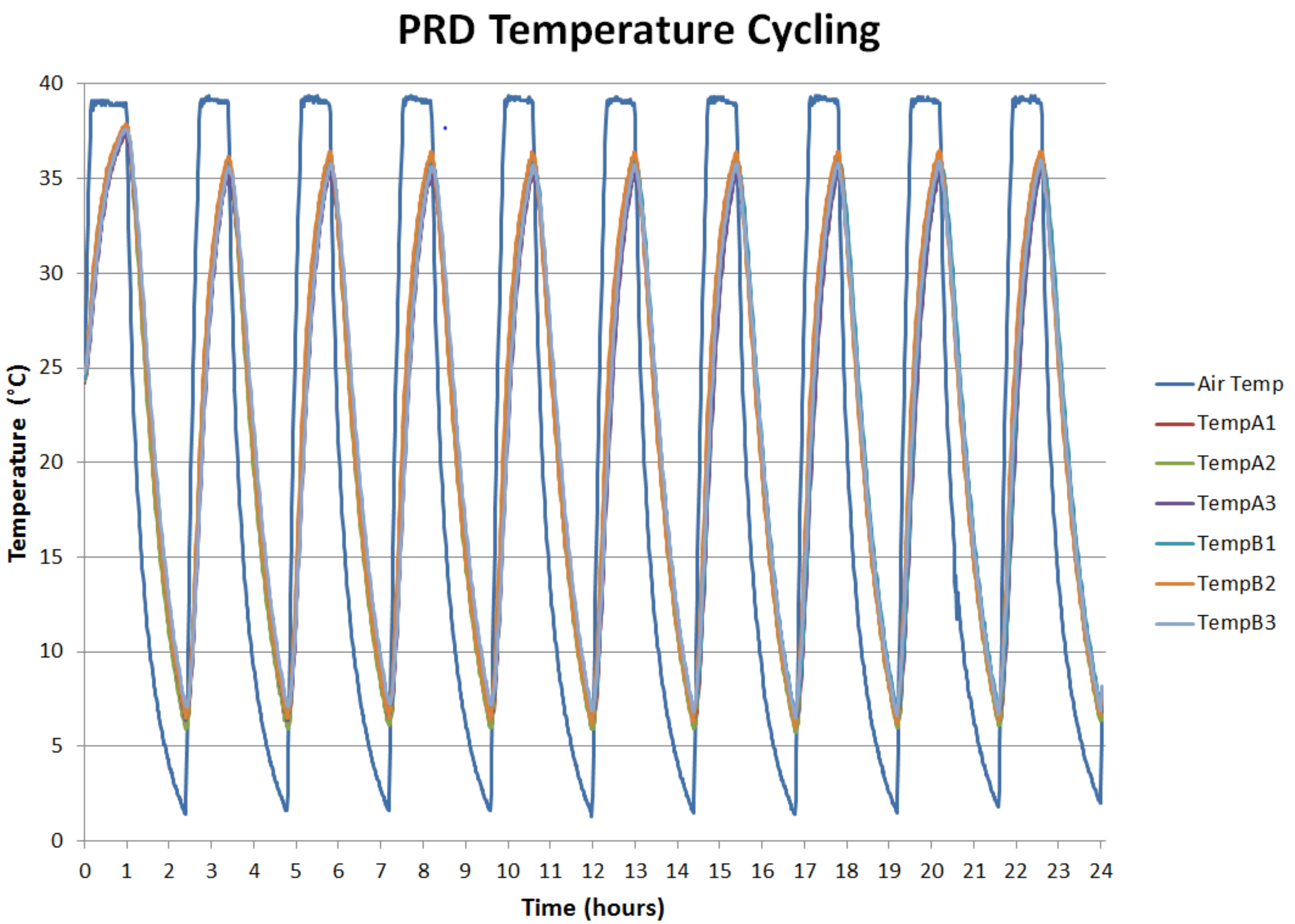


Relief valve nozzle S/N 586381 (NREL photo)



Relief valve nozzle S/N 586381 (NREL photo)

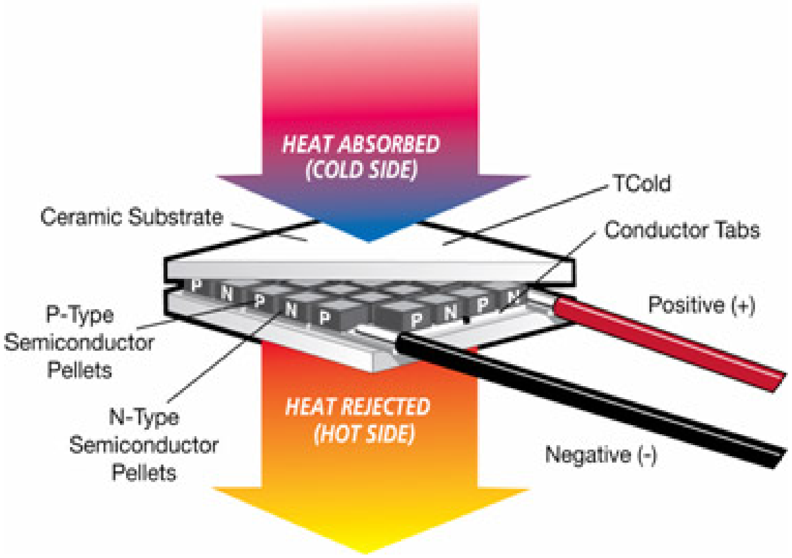
Accomplishments and Progress: Accelerated Life Cycle Test



Automated PLC temperature control provides repeatable and reproducible operation over the planned temperature extremes

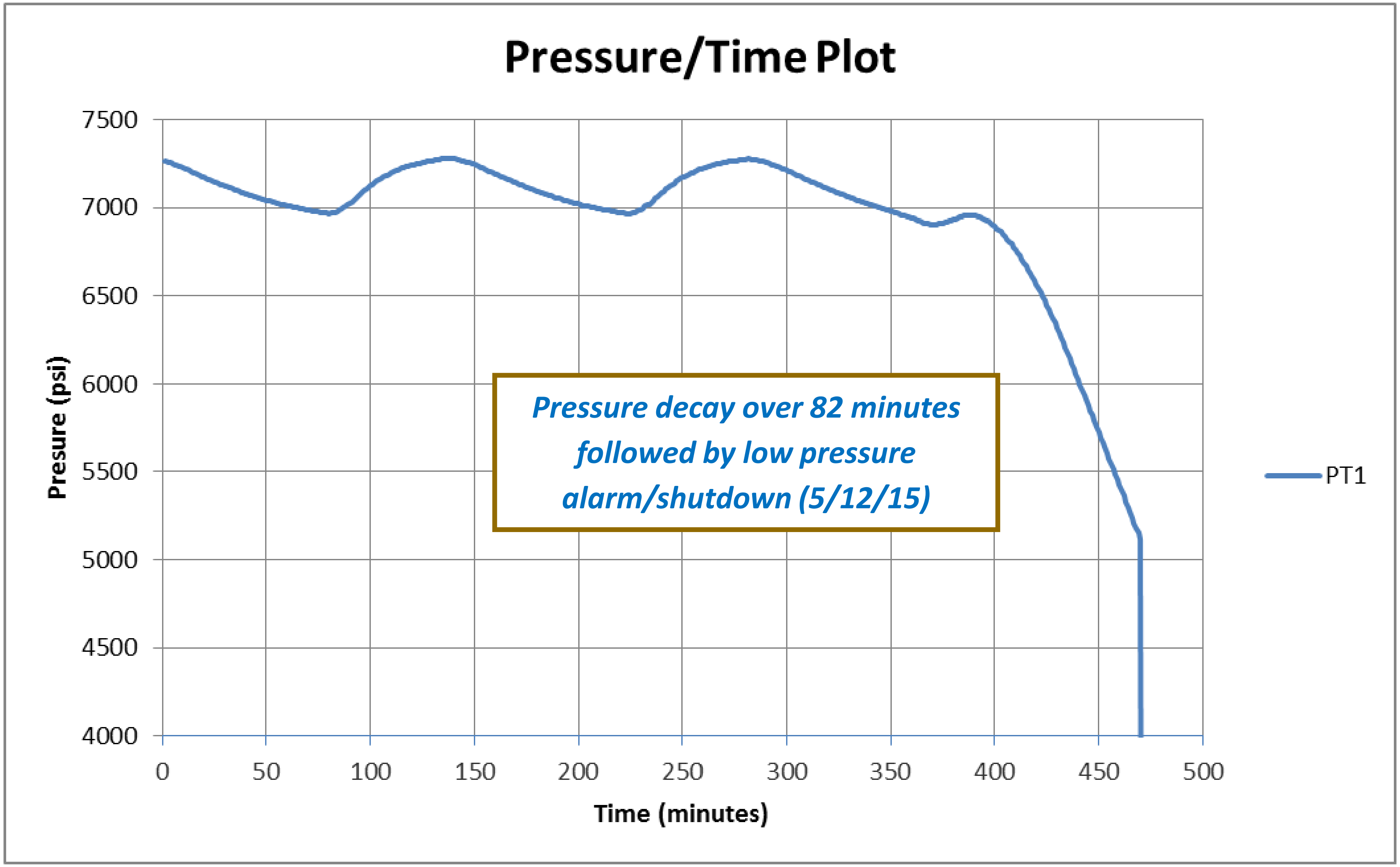
Accomplishments and Progress: Thermoelectric Device Operation Lesson Learned

- **TEC (Thermoelectric Cooler) was used for the thermal cooling cycle due cost effectiveness and simplicity of operation**
  - Can be used for heating or cooling
  - PRD operates with fixed heater, using TEC's for cooling only
- **Thermal cycling reliability lesson learned**
  - Use of a thermal grade epoxy created good conductive efficiency but fixed mounting created differential thermal expansion stresses that caused premature failure of semiconductor material
  - Alternate method of using Bellville spring washers with fasteners is preferred method for high cycle rate operation and is recommended for future component testing with thermal cycling



Lesson learned from thermal cycling testing root cause failure analysis: TEC failure is caused by differential thermal expansion between the brittle semiconductor material and the stainless steel base material

Accomplishments and Progress:
Relief Valve Reliability – Leak Failure



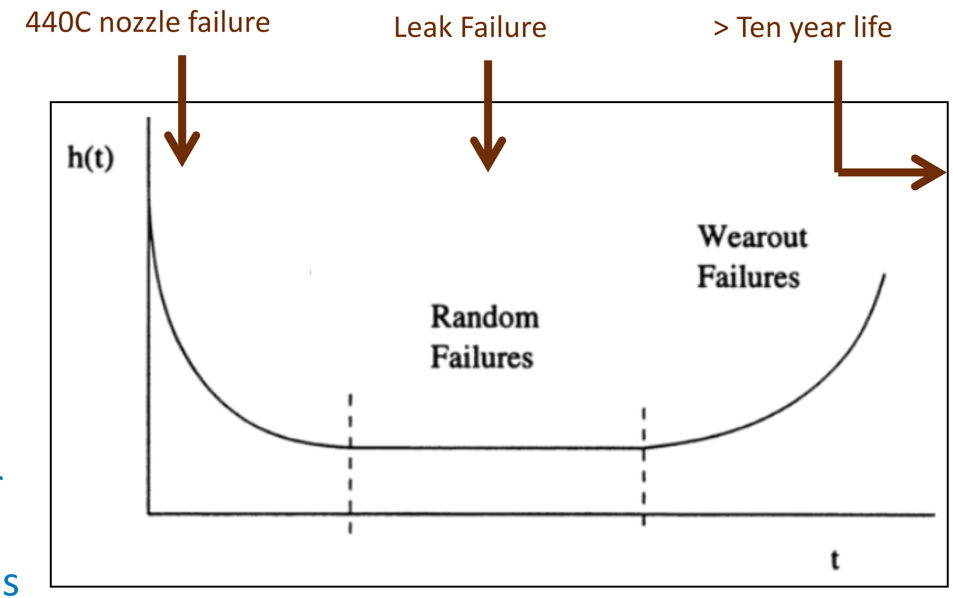
Upset condition encountered after 1200 cycles. Leak was detected in vent line. After depressurization and restart, valve was able to reseat and temperature cycle testing continued.

Accomplishments and Progress: PRD Test Results Summary

- **Two valves have survived laboratory thermal cycling equivalent to seven years of daily temperature cycles**
  - Additional 3 years of actual field operation
  - Total of 10 years equivalent operational cycling
- **How many cycles would be representative of end of life**
  - Maintenance interval for PRD’s is typically recommended as every three years
  - Maintenance includes resetting relief point by certified technician, includes repair kit replacing seals, nozzles and seating material
  - Ten years is more than three times maintenance interval and is being used as an end of life equivalent
- **Conclusion that ten years of end of life thermal cycling is not sufficient to duplicate 440C nozzle failure mode on two valves tested**
- **One failure was detected, the valve spuriously opening at pressure below the set point (Valve was able to reseat after vent down and re-pressure, no root cause was able to be identified)**

Accomplishments and Progress: PRD Test Results Summary

- **Two failures**
  - *Field Failure:* One valve showed a 440C nozzle failure, failing after eight months operation. The Sandia report identified contributing factors as improper material selection, possible preexisting condition (over torque) and out of specification hardness
  - NREL reliability testing showed leak failure, determined to be a valve spuriously opening, this failure is difficult to predict or control but is a known failure mode within the compressed gas industry (categorized as a random failure)
- **End of life results**
  - Two valves tested under this test project were subject to ten years equivalent operational life with no terminating failures, i.e. crack size and growth rates were below failure threshold (categorized as wearout failure - determined to be greater than ten years life based on two test samples)



Source: Klutke, Kiessler and Wortman, *IEEE Transactions on Reliability*, vol. 52, no. 1, pp. 125-129, March 2003

These test results show that PRD failure modes in hydrogen service don't originate from a single root cause. Understanding of fracture mechanics methods for failure prediction is important for component design in hydrogen service. Use of performance based component level tests may not reveal all insufficiencies for design qualification purposes.

Accomplishments and Progress: PRD Test Results Summary

Outcomes from the relief valve reliability test program are summarized:

- Component level testing to end of life conditions was not able to reproduce the 440C nozzle failure mode.
- Component testing has the capability to capture actual three dimensional stress profiles but is limited in capability to elevate stresses to failure. A specialty apparatus could be produced to test at higher pressures (and stresses). This could potentially gather data on crack growth rate in a component level environment and could be considered for future testing but is outside the scope of this project.
- Testing for hydrogen effects on materials at a component level can be considered an extension of the work Sandia is doing in hydrogen effect on materials testing. During component testing, no stress concentrations (notches) were added to the parts and the conclusion is that the elevated stresses were not sufficient to produce a failure. This is consistent with a fracture mechanics approach to prediction of failure.
- Hydrogen effects on materials, as being addressed in codes and standards, use an approach where materials are tested for hydrogen effects at the coupon level. This information is then being used for design by prequalifying materials that are used in a hydrogen environment. As shown by the component testing completed, testing for hydrogen effects on materials on a component level has limitations that preclude the use in certification testing.
- One failure was detected during the reliability test sequence. The pressure relief valve failed open, releasing pressure until a pressure safety was tripped in the controls, releasing pressure in the system. This spurious opening of the valve is unrelated to the 440C material selection and was not caused by hydrogen effects on materials however a root cause determination was not found.

Accomplishments and Progress: NREL PRD Failure Root Cause Analysis

- **At NREL's Wind to Hydrogen demonstration site, a PRD failed open, venting hydrogen, with no facility damage or injury**
- **The relief valve was located on a medium pressure 3000 psig stationary storage. The relief valve was set at a 4000 psig set point**
- **During venting, the relief valve reseated at a pressure of just a few hundred psi, venting down the majority of the hydrogen in the storage system with no incident.**
- **After removal from the system, the valve was sent to the manufacturer for root cause failure analysis**
- **The manufacturer first tested the valve and found that it relieved at ±3% of its set point (per ASME specification). The manufacturer was not able to reproduce the spurious opening that occurred during operation.**
- **After disassembly and inspection the manufacturer analysis was not able to determine a root cause of the failure. (these random failures are known to be an issue with relief valves and in general are not a serious safety concern, releasing hydrogen up a vent stack that is designed for this purpose)**

NREL's high pressure hydrogen production/storage/dispensing systems are used in cases like this to investigate failure modes that occur under real world operating conditions

Accomplishments and Progress:
NREL PRD Failure Root Cause Analysis (continued)

Potential Root Causes for PRD Spurious Opening

- ***Heating of a few hundred degrees can cause thermal expansion of the bonnet and relaxing of the spring. This heat could have been caused by a hydrogen leak at the base of the valve that found a spark and ignited. The hydrogen flame is difficult to see but could produce high localized temperatures.***
- ***Vibration/shock load on the valve could cause the valve to pop open. Once the valve is open, the gas flow is designed to keep the valve open, reseating at some point 10% to 20% below the set pressure. The loading could be caused a process/piping shock, water hammer, wind generated pipe harmonic or some other upset. There could also be some other external shock caused by impact from an unknown source. (note: failure to reseat could be caused by ice buildup as a result of thermodynamic cooling in the venting gas)***
- ***Particulate contamination could work into the seating area, causing the valve to crack open. Once the valve is open the gas flow could keep the valve open. Any evidence of particulate contamination could be flushed out by the flowing gas.***

Relief Device Root Cause Failure analysis will often be inconclusive, in this case the relief valve when vented down and pulled from service was able to relive pressure within ±3% of the original set point

Summary of Pressure Relief Device Failure Modes

Published literature search on relief valve reliability and safety risk was employed to identify failure modes. In many cases root causes for each failure mode are not well understood or quantified.

- **Failure to open: Valves can become stuck closed, testing at pressures as high as three times the set point have failed to open the relief valve**
- **Opens above set point: ASME code requires that relief valves open within ± 3% of the set point**
- **Stuck open: Once open, valves are designed to reseat at pressure below set point (valve hysteresis) but can remain in the open position**
- **Fails to relieve required capacity: Potential system design issue or vent line blockage**
- **Opens spuriously: Valves are know to open at pressures below the set point which creates unintended release of hydrogen**
- **Leakage: Seats can get damaged, non metallic materials age and can creep or pressure set. Added challenges exist at high pressure**

Valves opening spuriously are a known failure mode and can be an issue if the gas cloud release does not properly disperse and finds an ignition source

Reference: "Predicting Relief Valve Reliability, Results of the API Risk-Based Inspection and AIChE/CCPS Equipment Reliability Database Groups" Process Plant Safety Symposium, April 25th, 2001

Industry Collaboration: Compressed Gas Association

- **Release from a tube trailer PRD vent can result in a safety incident depending on the environment surrounding the release**
- **CGA completed testing of hydrogen tube trailers both with and without TPRD's to better understand the performance of these systems under an engulfing fire scenario. Results from that test program include the following:**
  - Even in the case where no TPRD was installed, there was no cylinder burst after an engulfing fire with 500 gallons of aviation fuel consumed in a fire that lasted 17 minutes
  - The engulfing fire created piping leaks that acted to relieve system pressure
  - Post test burst was conducted after the engulfing fire, results showing that burst pressures matched the new cylinder strength i.e. no degradation to overall material strength
- **Based on the results of the engulfing fire tests, CGA revised document CGA S-1.1 (2011 edition), removing requirements for a relief device when transporting hydrogen**
- **PHMSA (Pipeline and Hazardous Materials Safety Administration) in the code of federal regulation currently references CGA S-1.1 2005 edition, there is proposed rule making to reference CGA S-1.1 2011 edition. This update is waiting further support and possible R&D for changing federal code requirements**

Reference: "The Removal of Pressure Relief Devices from Compressed Gas Cylinders containing Flammable Gas.", Barlen and Associates 2013

Industry Collaboration

- Presentation at NFPA separation task group in person meeting on 11-11-15 to solicit feed back on PRD testing
- Proposal is being considered by CGA to form PRD task group under hydrogen technologies committee
- Independent discussion with industrial gas suppliers to determine path forward for PRD project
  - Gerry Sameth – CGA
  - John Anicello – Airgas (and CGA Board of Directors)
  - Dave Farese – APCI
  - Rob Early – Praxair
- Future work to consider would be to engage with ASME BPVC Section VIII committee to resolve issues with requirements for PRV’s on stationary hydrogen storage

Responses to Reviewer Comments

- “Modifying a component for failure by changing the material to one that is susceptible to fatigue crack growth does not add to the understanding of failure mechanisms…the example given by the principal investigator (PI) of exposing a composite overwrapped pressure vessel (COPV) to a qualifying test when the COPV has been exposed to acid to see whether the qualifying test will fail the tank (as it should) is of value.” – Using a performance based testing approach to product acceptance and certification relies on the ability of a component level test, as defined in a industry standard, being capable of failing an improper design or material selection. In both these examples, hydrogen attack of 440C material and acid attack of composite materials (glass and aramid), a capable test would fail the part. In the case of hydrogen attack, a performance based test is not capable of failing the part, as shown by the results of tests and understood from a knowledge of a fracture mechanics approach to hydrogen attack.
- “…does not mention the current efforts at the Compressed Gas Association to remove PRDs from hydrogen and all other tube trailers.” – The CGA work was a subject of discussion within the working group (as described in collaboration section) along with further dialog through one on one discussion and literature reference. There is agreement that this is a significant step in improving the codes and standards relative to the safety of high pressure hydrogen systems and the proper use of pressure relief devices. Supporting codes and standards is a primary focus of the component R&D project.
- “The style of the known valve PRD failure should be tested with pressure cycles.” – The known PRD field failure was on a fixed hydrogen storage system. These systems typically have very few pressure fluctuations but are exposed to daily temperature fluctuations. To verify the operating conditions, the engineering designer/operator was consulted to determine pressure settings that these PRD’s experience. Since this storage was supplying hydrogen for bus fueling, there is a desire to maintain storage pressure for back to back bus fills. The system is designed so that daily fill cycles are recorded and an algorithm is used to predetermine the compressor operational load so that pressure will be maintained within a fixed range throughout the back to back filling events. The conclusion was that although pressure cycling would be relatively simple to perform, it would not replicate the actual conditions under which these valves failed. Pressure cycling could be conducted in a future test. This would be valuable for a HALT (Highly Accelerated Life Test) type protocol where stressors are typically increased beyond typical operational values with the purpose of finding the weakest point in the design.

Proposed Future Work

- NREL is planning a QRA project for component safety to use the Sandia HyRAM model to integrate deterministic and probabilistic models into the application of pressure relief devices. This project will be conducted on a contract basis.
- NREL is starting a project to survey early station deployment to gather data on nozzle/receptacle interface issues. This project is utilizing CSA's expertise on ISO working groups and NREL's expertise in Technology Validation for secure data collection. Data will be collected to determine root cause of the issues and to define any needs for validation testing in support of standards development.
- Safety Codes and Standards has collaborated with the H2FIRST Hydrogen Meter Benchmarking project (funding support from Technology Validation) with the purpose of working toward systems that will meet the NIST Handbook 44 ±1.5% accuracy requirements for motor vehicle fuels.
- Continued support of hydrogen codes and standards with the goal of improved requirements for component safety such as supporting the PHMSA adoption of latest revision of CGA standards and engaging with ASME BPVC Section VIII committee to resolve issues with requirements for PRV's on stationary hydrogen storage.
- ESIF high pressure hydrogen test cell can be used for future component testing to extend the pressure relief device testing to higher stresses or with additional pressure cycling. The apparatus can be easily reconfigured to support future component testing needs. Testing of other high pressure components (valves, fittings, regulators, welded housings) can be conducted to provide reliability data for use by industry stakeholders.
- Extend pressure relief device testing to include non-metallic material testing at conditions experienced in a high pressure hydrogen environment.

Summary

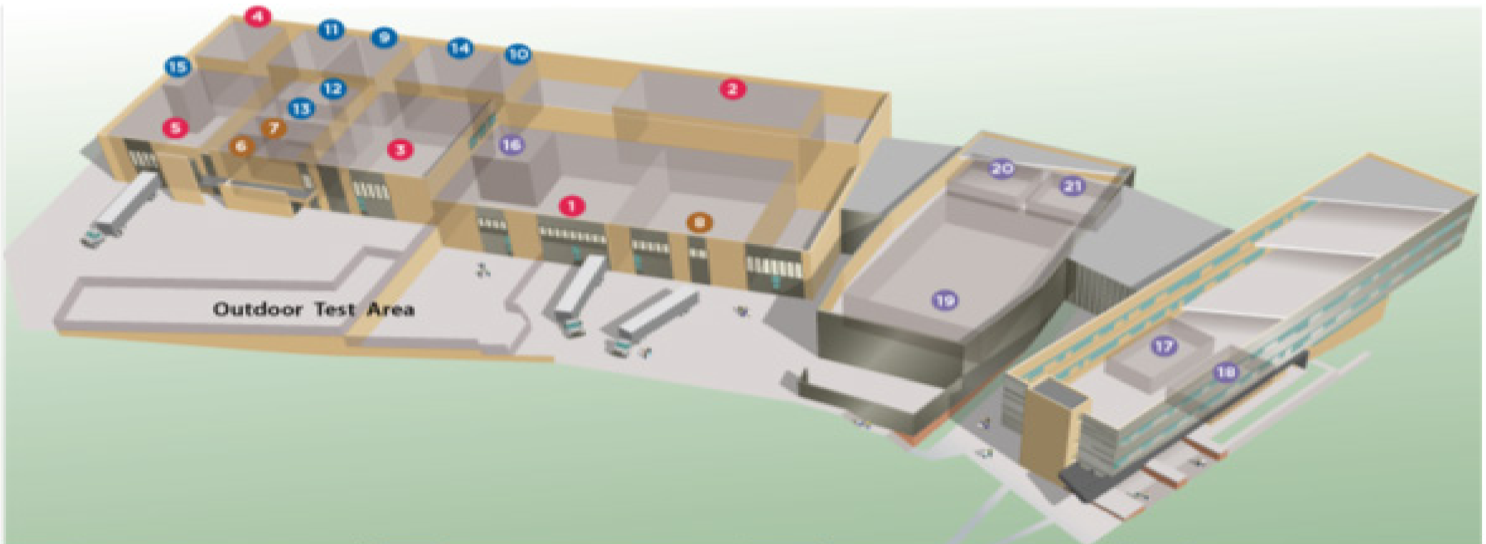
- **Provide R&D testing aimed at identifying root cause safety/reliability failure modes on high pressure hydrogen components and systems.**
- **Work with codes and standards technical committees to coordinate information exchange on early market system operation**
- **Collaborate with industry to provide feedback on high pressure hydrogen component and system issues.**

ESIF – Energy Systems Integration Facility
NREL laboratory facility provides laboratory space R&D testing of high pressure hydrogen component and system.

Technical Back-Up Slides

ESIF Component Test Utilization

Energy Systems Integration Facility



Electricity Laboratories

1. Power Systems Integration
2. Smart Power
3. Energy Storage
4. Electrical Characterization
5. Energy Systems Integration

Thermal Laboratories

6. Thermal Systems
7. Thermal Storage Materials
8. Optical Characterization and Thermal Systems

Fuel Laboratories

9. Energy Systems Fabrication
10. Manufacturing
11. Materials Characterization
12. Electrochemical
13. Energy Systems Sensor
14. Fuel Cell Development
15. High-Pressure Testing

Data, Analysis, and Visualization

16. ESIF Control Room
17. Visualization Room
18. Secure Data Center
19. High Performance Computing

- Component Testing Laboratory Capability within ESIF

Acronyms and Abbreviations

AIST: National Institute of Advanced Industrial Science and Technology

ANSI: American National Standards Institute

ASME: American Society of Mechanical Engineers

CDFA: California Department of Food and Agriculture

COPV: Composite Overwrapped Pressure Vessel

CSA: Canadian Standards Association

CSM: Colorado School of Mines

GTR: Global Technical Regulations

HALT – Highly Accelerated Life Test

HySUT: The Research Association of Hydrogen Supply/Utilization Technology

IEC: International Electrotechnical Commission

ISO: International Organization for Standardization

JRC: Joint Research Centre

NEDO: New Energy and Industrial Technology Development Organization

NFPA: National Fire Protection Association

NHTSA: National Highway Traffic Safety Administration

NRTL: Nationally Recognized Testing Laboratories

NIST: National Institute of Standards and Technology

PHMSA: Pipeline and Hazardous Materials Safety Administration

PLC: Programmable Logic Controller

PNNL: Pacific Northwest National Laboratory

SAE: Society of Automotive Engineers

SNL: Sandia National Laboratories