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Investigation of the Hydrogen Release Incident at the AC Transit Emeryville Facility

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Abstract

This report summarizes the investigation of the release of approximately 300kg of hydrogen at the AC Transit Facility in Emeryville, CA. The hydrogen release was avoidable in both the root cause and contributing factors. The report highlights the need for communication in all phases of project planning and implementation. Apart from the failed valve, the hydrogen system functioned as designed, venting the hydrogen gas a safe distance above surrounding structures and keeping the subsequent fire away from personnel and equipment. The Emeryville Fire Department responded appropriately given the information provided to the Incident Commander. No injuries or fatalities resulted from the incident.

ACKNOWLEDGEMENTS

Sandia National Laboratories' participation in this investigation is due in part to the ongoing support from the US Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technology Safety, Codes and Standards Program.

CONTENTS

1. Introduction.....	7
2. Background.....	9
2.1. Fueling Station Description	9
2.2. AC Transit in the Broader Context	10
3. Incident Description.....	11
4. Root Cause and Contributing Factors	13
4.1. Root Cause: Analysis of Failed Part	13
4.2. Contributing Factor: Timely communication of critical data	14
4.3. Contributing Factor: System Design.....	14
5. Recommendations.....	17
Appendix A: Metallurgical Investigation of Failed Pressure Relief Valve	19
A.1. Summary	19
A.2. Background and Preliminary Examination	19
A.3. Fracture Analysis Background.....	21
A.3.1. Hydrogen-Assisted Fracture Background	22
A.4. Analysis Method	23
A.5. Analysis Results.....	24
A.5.1. Visual inspection	24
A.5.2. Composition	24
A.5.3. Hardness	25
A.5.4. Metallography.....	25
A.5.5. Fractography.....	27
A.6. Conclusions	27
A.7. Test Protocol	28
A.7.1. Phase I: Non-Destructive Examination	28
A.7.2. Phase II: Destructive Examination	29
A.8. References.....	31
A.9. Biographical Information.....	32
External Recipients	33
Internal Recipients	33

FIGURES

Figure 1 Hydrogen system block diagram; location of pressure relief valve emphasis added.....	9
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1. INTRODUCTION

On May 4, 2012 a pressure relief valve at the AC Transit Facility in Emeryville, CA failed leading to the release of approximately 300kg of hydrogen. The hydrogen release was avoidable in both the root cause and contributing factors. The analysis in this report highlights the need for communication in all phases of project planning and implementation. Apart from the failed valve, the hydrogen system functioned as designed, venting the hydrogen gas a safe distance above surrounding structures and keeping the subsequent fire away from personnel and equipment. The Emeryville Fire Department responded appropriately given the information provided to the Incident Commander. No injuries or fatalities resulted from the incident.

The root cause, improper material selection in a sub-component of the pressure relief valve could have been avoided by clear communication and sufficient diligence during safety reviews. A contributing factor, lack of timely communication of critical system data, would have been avoided by adherence to written emergency protocols and improved remote measuring capability. Another contributing factor, lack of sub-system isolation within the storage design could have been avoided through proper communication during the hazard assessment portion of the project planning. Finally, the failure to communicate the addition of a canopy to the final station design, reduced the efficacy of the hydrogen venting apparatus resulting in scorching of the canopy. This report provides several recommendations for this station both as criteria for resuming operation and as continuing actions. Many of these recommendations are applicable to similar fueling stations: in operation, in construction or in planning.

This report contains four sections: background, incident description, detailed discussion of root cause and contributing factors, and recommendations. An appendix is provided that summarizes a metallurgical analysis of the failed valve.

The station was designed by Jacobs Engineering and Linde and constructed by W.L. Butler. The District placed it in service on August 31, 2011 and has fueled more than 1,036 times before this, the first incident.

2.2. AC Transit in the Broader Context

Hydrogen fuel for electric drive vehicles using a fuel cell for conversion of chemical to electrical energy has grown in use over the past few years. Much of the growth has occurred in heavy duty and industrial vehicles. There are approximately 500 light-duty, 250 heavy duty and 3000 industrial fuel cell powered electric vehicles operating in the world today.

Emeryville is not unique in either size or population density to many other refueling operations. There are over 50 hydrogen fueling stations for light and heavy duty vehicles in the United States, and internationally, there are over 150 stations open with more than 100 stations in the planning stages².

There is a strong history of safety in the use of hydrogen. Beyond fueling stations hydrogen is widely used for specialty processes such as microchip manufacturing, heat treatment, food processing and refineries. Accidents involving hydrogen vary, often circumstances rather than the fuel itself is the root cause of the incident. The website: www.h2incidents.org is a valuable resource for both hydrogen incident descriptions and industry best practices.

Industry best practices have been adopted in hydrogen vehicle specific product standards and specific chapters added to model fire and building codes. These codes and standards have been updated recently to further support the construction of hydrogen fueling stations and the deployment of fuel cell powered electric vehicles.

² Number of stations based on data provided in files accessed from <http://hydrogen.pnl.gov/cocoon/morf/hydrogen/article/707> as well as input from informed sources. Numbers provided are intended to represent relative number of stations to place the Emeryville station in context rather than provide specific data, particularly the number of “planned” stations.

3. INCIDENT DESCRIPTION

The incident started at approximately 7:45AM on May 4, 2012. A pressure relief valve failed causing the release of approximately 300 kg (790lbs) of hydrogen and eventually evacuating many local businesses and schools. The following describes the incident from a collection of emergency response log, system data acquisition, communication records and witness accounts.

At 7:45AM, the nozzle sub-assembly portion of the pressure relief valve fails causing an immediate release of approximately 30 kg of hydrogen in the first minute. This rapid release of hydrogen mixed with air in the vent tube, this mixture subsequently ignited producing the loud “boom” reported by eye and ear witnesses. After the pre-mixed gases were consumed the venting hydrogen produced a jet flame emanating from the outlet of the vent system. The flames from this vent impinged upon the top of the canopy of the manual dispenser causing the paint and dust on the canopy to combust. The combusting paint and dust likely produced the yellow flames and smoke reported by eye-witnesses. Eye-witnesses reported that the yellow flame disappeared after an unspecified time; ‘self-extinguishment’ would be consistent with the canopy materials (painted metal).

Immediately after the valve failed, emergency services were contacted by phone and fire alarm pull stations. Initial reports summarized by emergency log as “possible building fire and explosion”. Emeryville Police Department then updated the responding units that this was a possible hydrogen event. Meanwhile, consistent with written procedures, an AC Transit employee activates an emergency stop for the hydrogen station. The emergency stop closes several valves located at key points throughout the system. This action isolated the incident to the high-pressure storage tubes, preventing the venting of all of the site’s hydrogen.

At 7:57 AM, after a primary search, Emeryville Fire Department (EFD) units classify the incident as, “AC Transit fuel tank on fire.” Meanwhile, the Linde automated system, Sencaphone, notifies a technician who remotely accesses system information. Gas pressure in the system has decreased to 1/3 operating pressure, approximately 1/2 of the stored gaseous hydrogen has released. No liquid hydrogen has been, nor will be released in the event.

At 8:08 AM, in accordance with emergency response procedures, EFD contacts Linde National Operations Center (NOC). Linde NOC does not provide information regarding the condition of the system to EFD.

At 8:17 AM, AC Transit Building evacuated.

At 8:20AM, 8:24, 8:25 Linde system reports low pressure alarms for “high” pressure, “medium” pressure and “low” pressure gaseous hydrogen cascade storage systems respectively. These low pressure alarms indicate that the majority of gas has vented from the systems. Remaining hydrogen is isolated to compression, liquid tank and interconnection process plumbing. Audible and visual indications would still lead EFD personnel to believe the situation was continuing to escalate, despite system conditions.

At 8:40 AM, EFD personnel reach AC Transit point of contact, by phone. No information on the condition of the system is provided to EFD by AC Transit contact.

At 8:58 AM, EFD contacts Linde NOC. NOC advises EFD that Linde personnel are en route. No information on the condition of the system is provided to EFD by the Linde NOC.

Around 9:00 AM, the Emeryville Secondary School is evacuated and Anna Yates Elementary School is asked to shelter in place.

At 9:06 AM, EFD and AC Transit personnel use AC Transit security cameras to remotely observe the site.

At 9:20 AM, EFD video surveillance survey reports multiple release points. A report that proved erroneous in the post-incident investigation.

At 9:30 AM, Linde personnel arrive but are prevented from entering scene to communicate to the incident command

At 9:47 AM, EFD evacuates a 1 block radius.

At 10:00 AM, EFD, Linde and AC Transit personnel enter the area with thermal imaging equipment. Confirm vent stack fire, no impingement on gaseous or liquid containers. Meanwhile, Incident Command reports situation is stabilized.

At 10:12 AM, Linde personnel close isolation valve on leaking vent stack.

At 10:58 AM, Incident Command terminated. End of incident.

4. ROOT CAUSE AND CONTRIBUTING FACTORS

4.1. Root Cause: Analysis of Failed Part

The root cause of the incident was a failed pressure relief valve. Relief valves are required by plumbing and piping codes on stationary storage systems. These relief valves are designed to release gas in the event of an overpressure condition in the storage system. The type of valve used, a spring-operated, reseating pressure relief valve, is common to many compressed gas applications.

There is no evidence that AC Transit's system exceeded any of its pressure limits before or during this event. Evaluation of the failed valve component does not conflict with the conclusion that overpressure was not a contributing factor to the valve failure.

Sandia National Laboratory (Livermore, CA) conducted an extensive metallurgical analysis of the failed valve. Details from the analysis are provided in Appendix A. The analysis concludes that improper material selection and deviations from valve production processes lead to the valve failure³.

Proper material selection would have prevented this incident. The valve manufacturer already offers the same valve component using an appropriate material, therefore the correct selection available. Further, widely accepted best practices should have led to the correct specification of the valve material.

All safety reviews must thoroughly evaluate the materials used in all components; particularly safety critical components to ensure the components meet the design pressure and service environments for the application. The valves used on the AC Transit system met the pressure requirements; however the material selected for the nozzle sub-assembly, 440-C stainless steel, was a poor choice for hydrogen applications.

The use of high strength steels is not recommended for components which contact hydrogen ('wetted components'). Type 440-C stainless steel is one of several high strength steels which demonstrate extremely poor resistance to hydrogen and should not be used, as well documented in related literature. Also, the manufacturer's catalog lists components for this type of pressure relief valve that replaces this susceptible steel with type 316 stainless steel. Type 316 austenitic stainless is highly resistant to hydrogen embrittlement.

Much of the root cause and contributing factors in this incident are the results of miscommunication. With regard to improper materials, safety reviews of components and verification of part numbers for specific safety vulnerabilities, such as relief valves, is a common practice in both engineering and safety communities. Communication during these reviews

³ The appendix provides further detail regarding deviation in the production of the valve, specifically the failed valve component's hardness, a measurement of the material's strength.

along with attention to material selection details by: vendors, sub-contractors, general contractors and station managers, would have prevented this incident.

4.2. Contributing Factor: Timely communication of critical data

Lack of timely information regarding the status of the system contributed to the escalation of the event. During the event, the Incident Commander responded appropriately to the information provided. Unfortunately the AC Transit and Linde response during the incident deviated from written procedures subsequently; information was not available in a timely manner to the Incident Command. Providing additional information about the conditions of the station equipment and processes will allow future first responders to tailor the response with greater refinement.

Information regarding the status of the gas storage system was available when the Linde technician logged onto the remote monitoring system approximately 15 minutes after release started. Had that technician been able to contact the EFD Incident Command, the technician would have been able to describe the decreasing pressure in the gaseous storage and the stable condition of the liquid system. These facts would have proved invaluable to the Incident Command decisions. Unfortunately this information was not relayed to the incident command until approximately 10:00 AM; 2 hours 15 minutes after the incident began.

A communication and event timeline was constructed by the investigation team. The timeline shows that both AC Transit and Linde communicated well internally but failed to communicate with each other or the incident command until far into the incident.

The fire alarm system was not functional in the hours leading up to the incident due to maintenance initiated earlier that morning. Fire alarm personnel, working on the fire alarm system disabled the system that morning without contacting the fire department, a violation of written procedures. The status of the fire alarm system did not contribute to the incident nor did the status of the automatic fire monitoring system delay notification of the fire department.

4.3. Contributing Factor: System Design

The system design contributed to the escalation of the incident, specifically the location of vent outlets in relation to nearby canopy material and the release of the entire gaseous storage through a single point.

The relief valve system is designed to provide pressure relief for each storage container or “tube.” When activated the pressure relief is directed to specifically designed ventilation plumbing (“vent stacks”). Hydrogen has low ignition energy, which means that it ignites or catches fire readily, for instance due to static electricity or friction from particulates⁴. These vent

⁴ The topic of hydrogen “self-ignition” is an area of study and discussion in the scientific community. This analysis neither purports nor intends to determine the source of ignition in this incident. There is sufficient indication from the damaged canopy, ear and eye-witnesses that a flame was present.

systems are designed to safely relieve hydrogen regardless of whether the hydrogen subsequently ignites or not.

The vent system was not located sufficiently above the nearby canopy. The vent system is designed to release hydrogen safely regardless of ignition (CGA 5.5 section 5.3). According to hydrogen vent system standard, the vent system should be high enough to prevent impingement on personnel, equipment and other structures (CGA 5.5 section 6.3.1). The AC Transit station design should be evaluated against this requirement. During the incident, the paint on this canopy combusted and caused a secondary flame (yellow flame and smoke) which some eye-witnesses reported. The investigation revealed that this canopy was added to the station design but its location was not reviewed in relationship to the vent. This oversight contributed to the eye-witness report of fire and concern of secondary exposures as hydrogen flames are invisible or very light blue in color.

The system design did not isolate the fuel to a sub-set of containers (“tubes”). The failure of the system to isolate container meant that the failure of some of the pressure relief valves, those in the “high bank,” could subsequently relieve all of the gaseous storage 350 kg (790 lbs.). Thus the incident released more fuel and the release continued longer than if process isolation had been in place.

The audible indication (noise) of the gas release was the only indication of the status available to the first responders (see above comments on miscommunication). Since the audible release lasted longer, the first responders continued to escalate the incident.

The “AC Transit Hydrogen Fueling Station Emergency Action Plan” states that the system contained flame arrestors. This was later determined to have been an oversight in the creation of the document as flame arrestors were not installed on the system. It should be noted that flame arrestors are not required by code and that these devices do not prevent flames at the vent outlet but rather prevent the flame from continuing upstream to the containers.

It is not clear that the flame detectors identified the flame at the vent outlet. The location and detectability of the current flame detectors should be further evaluated.

5. RECOMMENDATIONS

The investigation team recommends the following actions:

- 1) Replace pressure relief valves with devices specifically designed for hydrogen service
 - a) A pressure relief valve component material exists in the manufacturer's catalog that replaces type 440-C with type 316 stainless steel. Type 316 austenitic stainless steel is used extensively in gaseous hydrogen systems.
 - b) An analysis of the materials used in components throughout the system should be conducted.
- 2) Update communications plan relative to all responsible parties. In particular establish process responsibility or "ownership" to better centralize the flow of information. Ensure that the process owner is easily identified by first responders and is free from other administrative emergency response duties to sufficiently support the liaison between the Incident Commander and the technical support.
 - a) Add information systems as appropriate to provide reliable system information to the Incident Commander.
 - b) Ensure critical data is accessible by emergency response call centers (for example, Linde's National Operations Center)
- 3) Update training documentation based on timeline analysis.
- 4) Perform refresher training and "table-top" or similar drills with key personnel designated to respond to the hydrogen station. Incorporate continuous improvement principles to evolve from a specific hydrogen team to accepted cultural norm within standard job functions.
- 5) Evaluate and implement the vent systems relative to the canopies and other equipment, ensure relief vent outlets are sufficiently above and oriented away from vulnerable equipment. Consider alternate materials of construction (paint on canopy) if unable to relocate vent outlets.
- 6) Evaluate and implement process system improvement taking advantage of opportunities to isolate sub-sets of the storage system.
- 7) Evaluate and implement changes to fire detection systems to identify hydrogen flames on the system.

APPENDIX A: METALLURGICAL INVESTIGATION OF FAILED PRESSURE RELIEF VALVE

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Prepared for: AC Transit, California Air Resources Board, and the city of Emeryville in support of AC Transit Hydrogen Incident Investigation; funded by the California Air Resources Board

A.1. Summary

The nozzle subassembly component of the pressure relief valve that failed appears to be manufactured from type 440C martensitic stainless steel; this type of steel is extremely embrittled by hydrogen and is a poor choice for service hydrogen-containing environments. Several factors may have contributed to enhanced susceptibility of this nozzle to hydrogen embrittlement: (i) significant external damage was observed on the nozzle, presumably incurred during assembly of the pressure relief valve, and (ii) the failed nozzle appears to be improperly heat treated since its hardness is significantly greater than the same part from another PRD from the same installation. The analysis was conducted using low-magnification (20x) visual inspection of the components, high-magnification electron microscopy of the fractured parts, qualitative compositional analysis, hardness evaluation and metallographic analysis of the failed material, as well as comparison of the components to parts from a functioning valve from the same system.

A.2. Background and Preliminary Examination

On May 4, 2012, the Emeryville Fire Department responded to a hydrogen release and fire at the AC Transit Hydrogen Fueling Station in Emeryville CA. Preliminary investigation determined that one of the pressure relief valves on the gaseous hydrogen storage system had failed. The failure was such that the integrity of the body of the pressure relief valve was maintained and gaseous hydrogen was released into the vent, consistent with the design of the system. The failure, however, prevented the pressure relief valve from closing, thus allowing venting of gaseous hydrogen to relatively low pressure.

The pressure relief valve was removed from the system and taken to a local valve repair shop. Upon disassembly of the failed pressure relief valve, it was determined that the nozzle subassembly had failed as shown in Figure A1. After this preliminary examination, the pressure relief valve components were sealed in plastic bags and transferred to Linde Corporation's Richmond CA facility for storage.

On May 29, 2012, a meeting was held at Linde Corporation's Richmond, CA facility to discuss the pressure relief valve failure. The sealed bag containing the failed pressure relief valve parts was opened for inspection by all attending parties. Inspection of the pressure relief valve nameplate indicated that the pressure relief valve was manufactured by Mercer Valve Co. in September 2010, Part No. 91-M6C61P1941QD and the activation pressure of the pressure relief

valve was set to 7777 psi. This part number represents standard gas service according to the manufacturer's website. Additionally, the manufacturer's catalog lists a PRD configuration from the same product family for sour gas service (with a nozzle and disk of 316 stainless steel); sour gas can induce hydrogen embrittlement in metals.

Figure A2 shows the internal components of the pressure relief valve: the two broken pieces of the nozzle subassembly (marked A1 and A2), the inlet base (marked B), the disk subassembly (marked C), and the set spring (marked D). The representative from Mercer Valve at the May 29th meeting identified the materials of construction of these pieces: the nozzle (A1 and A2) is 440C martensitic stainless steel; the inlet base (B) is 316 austenitic stainless steel; the disk subassembly (C) consists of a nose piece from 440C martensitic stainless steel, centering guide of 6061 aluminum, and shaft; and the set spring (D) is 17-7PH semi-austenitic stainless steel.

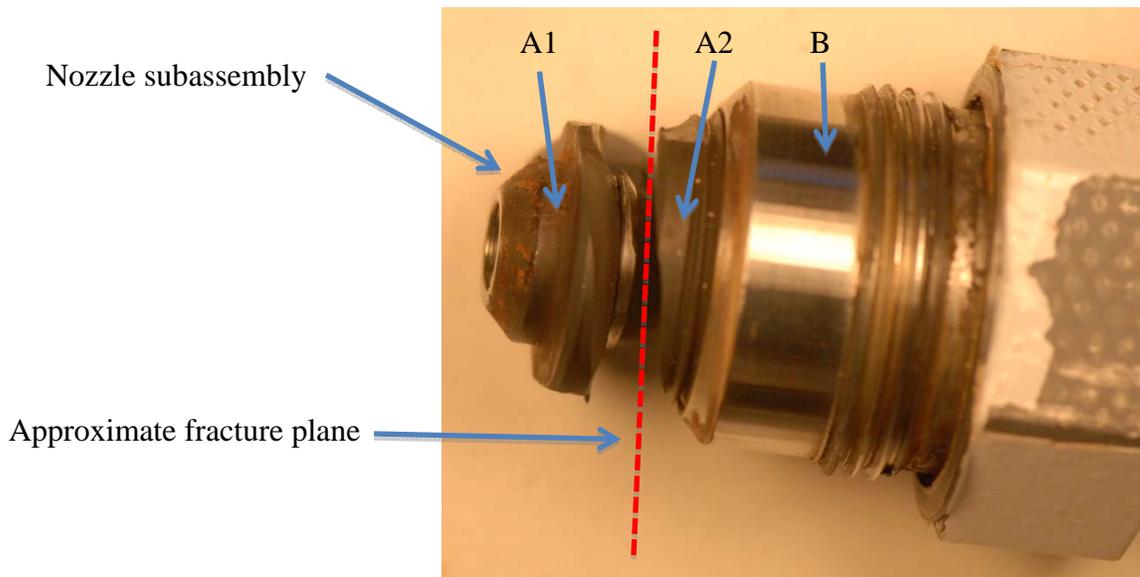


Figure A1. Failure of nozzle subassembly (A); nozzle subassembly is threaded into the inlet base (B).

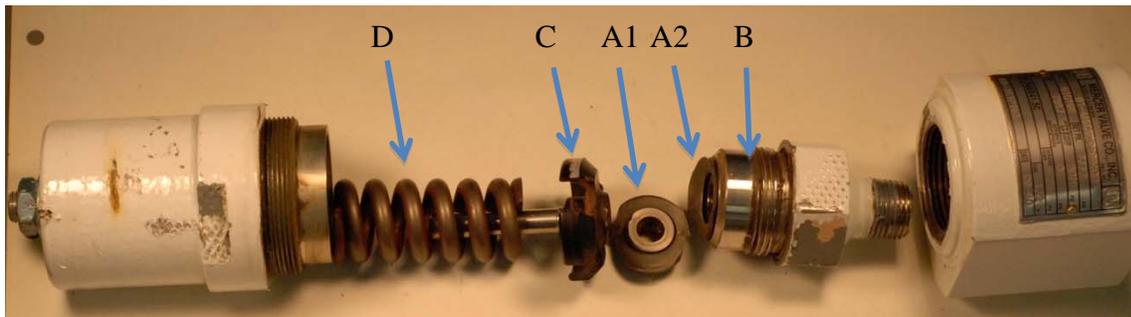


Figure A2. pressure relief valve components: failed nozzle subassembly (A1 and A2); inlet base (B); disk subassembly (C); set spring (D).

Details of the construction and function of the nozzle subassembly (the failed part) were not discussed at the May 29th meeting. The nozzle subassembly (A1 and A2) consists of several components. The nozzle housing or body is the piece that failed and is designed from type 440C

martensitic stainless steel. The other components of the nozzle subassembly are other materials, the details of which are presumably proprietary. Thus, the following discussion is restricted to the failed piece, which will be described as the nozzle.

A.3. Fracture Analysis Background

Structural failures occur when the stress in a material exceeds the ability of the material or structure to withstand the applied loading condition. One class of failure, termed fracture, occurs when a crack develops in material and reaches some critical size. Fracture initiates at defects in the material or at stress concentrators in the structure, e.g. sharp corners locally amplify the stress in the material, often initiating a crack at a defect in the material. Consequently, the initiation of cracks can often be traced back to materials defects and/or sharp corners (i.e., windows on aircraft are rounded to prevent the initiation of cracks at these locations).

Fracture usually consists of several competing processes, which can be idealized as brittle in one extreme (a dropped coffee cup) and as ductile in the other extreme (a paperclip that is bent repeatedly until it breaks). Brittle materials have low defect tolerance, meaning a small flaw (such as a scratch) can initiate a crack. Ductile materials, on the other hand, have high defect tolerance; in short, ductile materials can withstand external damage (as well as manufacturing defects). Metals are used in structural applications because they have high defect tolerance.

Austenite and martensite refer to the crystal structure of the metal. Common austenitic stainless steels (such as type 316 and 316L) are nominally single-phase austenite. In general, austenitic stainless steels are relatively low-strength alloys used for their excellent combination of corrosion resistance and formability. Type 316 austenitic stainless steels, in particular, have good resistance to hydrogen embrittlement and are used extensively in gaseous hydrogen systems. The martensitic stainless steels (such as type 440C) are used where high-strength is required in combination with some corrosion resistance. Martensitic alloys are typically formed or machined in the low-strength condition and then subjected to thermal treatment (technically referred to as quench and tempering) to achieve the desired martensitic crystal structure and high strength. The martensitic stainless steels are known to be sensitive to hydrogen embrittlement [2] and generally not recommended for hydrogen service [3].

Fracture events can be probed with a variety of tools depending on the nature of the event. Low-magnification optical microscopes aid determination of the orientation of fracture relative to the structure of the failed component. High-magnification electron microscopes are used to analyze the characteristics of the fractured surfaces, which often can be correlated with known fracture processes (e.g., ductile versus brittle fracture).

The characteristics of the material also provide important information about the expected strength and fracture behavior of materials. The fine-scale structure of the material, typically referred to as the microstructure, is probed by polishing sections of the material. Electron microscopes can also be used to determine compositional differences and other characteristics of the materials (such as crystal structure), which also provide important information about the quality of the materials. Hardness measurements (usually on polished sections of materials) provide information about the strength of materials as well as its quality relative to its expected

behavior. These tools represent the primary means for metallurgical analysis of structural failures.

A.3.1. Hydrogen-Assisted Fracture Background

Hydrogen has the unique characteristic that it dissolves into most metals. Although there are many processes resulting in hydrogen “up-take” in materials, in the context of gaseous hydrogen exposure of metals, hydrogen interacts with the surface usually forming atomic hydrogen prior to diffusing rapidly into the bulk of the metal. The surface characteristics of metals can strongly influence this process and mediate hydrogen “up-take” into the metal; however, these surface processes are extremely difficult to control, which may account for failures that appear to occur after prolonged exposure. Once dissolved into the metal, hydrogen segregates to areas of high stress, can strongly affect the ductility of the metal and can promote cracking. Because hydrogen reduces ductility, the term hydrogen embrittlement is often used (although it is important to note that even with large reductions in ductility, many “embrittled” metals remain ductile). The magnitude of hydrogen embrittlement depends sensitively on the combination of the (i) characteristics of the material, (ii) environmental conditions and (iii) mechanical loads (i.e., stresses) on the material. All metals are affected by hydrogen to some degree: some metals are negligibly affected by dry gaseous hydrogen (such as aluminum, although severely affected by hydrogen from corrosion processes), while other metals are severely affected by exposure to low-pressure gaseous hydrogen (such as high-strength steels). Metals that are strongly embrittled by hydrogen can be safely used as long as the design takes into account the reduction of ductility (e.g., by minimizing the stress in the component).

Hydrogen embrittlement, as mentioned above, depends on the (i) material, (ii) environment, and (iii) stress, thus changes to any of these variables can create a condition where a component becomes susceptible to the effects of hydrogen. For example, many transportable gas cylinders are manufactured from the same pressure vessel steels whether for use with nitrogen or with hydrogen; however, these cylinders are manufactured such that the steel has a relatively low strength. It is well known that if the strength is increased sufficiently, these steels can fail due to hydrogen embrittlement [4-7]; consequently, US Department of Transportation specifically disallows transportation of gaseous hydrogen in pressure vessels manufactured from high-strength steels (49CFR173.302a). In short, extrapolation to combinations of material, environment and stress outside the range of experience or engineering data can result in an undesirable outcome.

Many of the general trends of gaseous hydrogen embrittlement are embodied in Figure A3. This plot shows hydrogen resistance as a function of strength for a wide range of structural metals; a value of one indicates no measurable effect of gaseous hydrogen, while a value of zero indicates severe effects of hydrogen and implies brittle fracture. The alloys with high resistance to hydrogen embrittlement include relatively low-strength alloys such as austenitic stainless steels, aluminum, and copper. Materials with low resistance to hydrogen embrittlement include alloys in high-strength conditions.

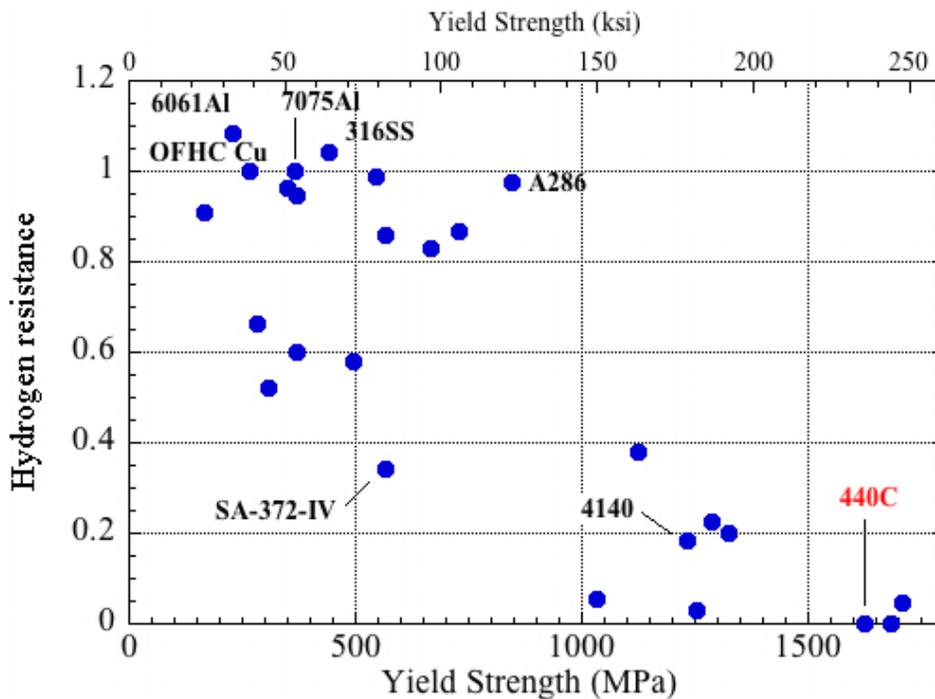


Figure A3. Hydrogen susceptibility as a function of yield strength for a range of structural alloys. The susceptibility is the ratio of reduction of area in a tensile test measured in gaseous hydrogen at pressure of 69 MPa relative to measurement in helium at the same pressure. All data from Reference [1].

A.4. Analysis Method

The protocol for the investigation is provided in Section A.7. In brief, the parts were examined visually and with the aid of low-magnification microscopes (up to 40x). The fracture surfaces were examined by scanning electron microscopy (SEM); qualitative compositional analysis was performed by energy dispersive spectroscopy (EDS). A metallographic (i.e., polished) section of the nozzle was prepared by sectioning a portion of the broken nozzle, and examined for microstructure. Microhardness measurements (Vicker's indenter) were performed on the polished section.

Additionally, a functioning pressure relief valve taken from the fueling station was disassembled at Sandia and the nozzle examined. A metallographic section was prepared for microstructural analysis and microhardness was measured at the same time as for the failed nozzle. All metallurgical investigation was conducted at Sandia National Laboratories in Livermore, CA.

A.5. Analysis Results

A.5.1. Visual inspection

Visual inspection shows that the nozzle failed across its largest diameter, in the vicinity of the wrench flats on the nozzle (which are used for inserting the nozzle subassembly into the base inlet). The basic dimensions of the part appear consistent with the functioning part. After sectioning part B1, the thread roots of sections A2-1 and A2-2 were carefully examined with a stereomicroscope. Evidence of secondary cracking at the thread root and machining “corners” could not be found. Inspection of the wrench flats, however, showed evidence of external damage (Figure A4a), presumably due to assembly. The polished cross sections suggest that the macroscopic crack can be associated with the internal corner in the nozzle as shown in Figure A5.

Similar inspection of the nozzle from the functioning pressure relief valve was also performed. There was no evidence of damage on this part, including undamaged wrench flats (Figure A4b).

A.5.2. Composition

Destructive compositional analysis was not performed. Qualitative compositional analysis was performed by EDS on the fracture surfaces, which revealed iron and chromium as the primary constituents, with chromium in the range of approximately 15-20 wt% relative to an iron base. This is consistent with type 440C martensitic stainless steel; ASTM A276 specifies this steel as 16-18 wt% chromium and nominally 1 wt% carbon with residuals (<1 wt%) of molybdenum, manganese, and silicon. High quality EDS could not be achieved due to the lack of cleanliness of the fracture surfaces.



Figure A4. Wrench flats on the (a) failed nozzle and (b) the functioning nozzle. Significant external damage is apparent the failed nozzle, while no damage is observed on functioning nozzle.

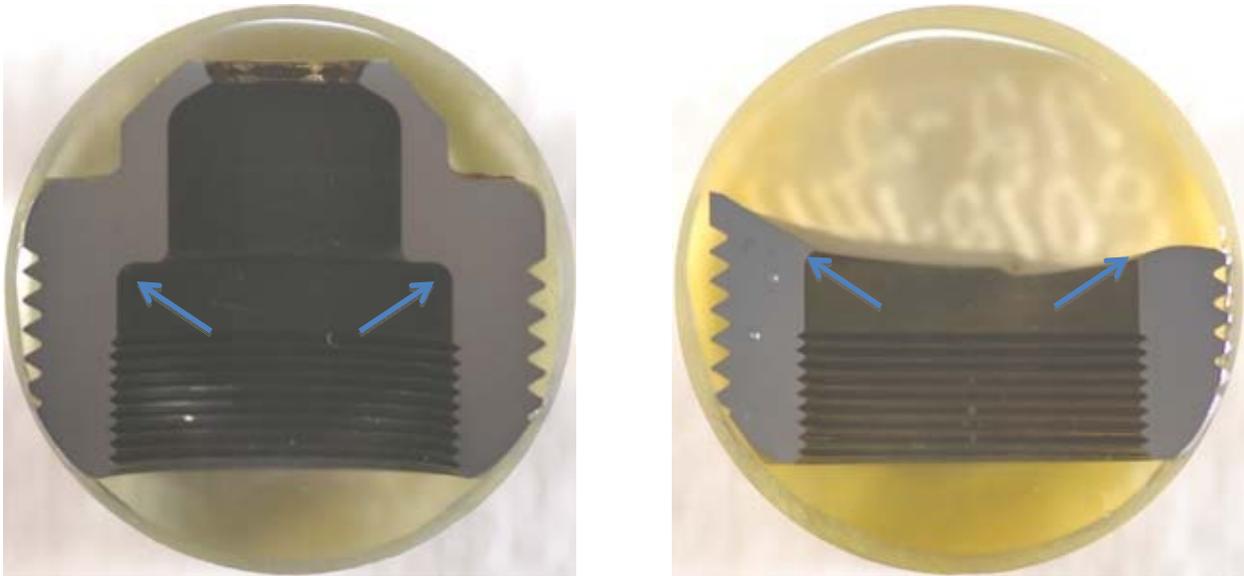


Figure A5. Polished cross sections of (a) functioning nozzle and (b) failed nozzle. The arrows indicate the internal corner associated with failure of the nozzle.

A.5.3. Hardness

Microhardness was measured using a Vicker's indenter and a load of 500 gram. Measurements were performed on the polished sections prior to etching. Before and after indentation of the specimens, a hardness standard was also measured. The standard is specified as 703 HV, and the measurements were 725 and 729 HV (before and after respectively). The average of three measurements on the fractured nozzle was 600 HV, while the average hardness from the functioning nozzle was 501 HV. The variation in the three measurements on the same material was less than 4 HV.

Rockwell Hardness Scale C (HRC) represents the common macrohardness scale used to specify the required hardness of high-strength steel, such as type 440C (typically specified as a range of about ± 2 HRC). The HRC, however, could not be measured on the polished sections due to the size and configuration of the part. Approximate conversions from HV to HRC using ASTM E140 Table 1 give approximately 55 and 49 for the failed and functioning nozzle respectively.

The yield strength of the material can be estimated from HV, where the yield strength is 1/3 of the hardness (using the proper unit conversions). While such correlations cannot be relied upon for accurate yield strength determination, such estimates provide information about the strength level of the material. The yield strength of the failed nozzle is estimated to be near 1960 MPa (280 ksi), while the yield strength of the functioning nozzle is estimated as 1640 MPa (240 ksi).

A.5.4. Metallography

The metallographic sections were examined prior to etching to allow examination of the profile of the nozzle and inspection of the thread roots at high magnification. Evidence of secondary cracking at the notch root was not found (Figure A6), consistent with the visual inspection. There appears to be some decarburization on the surface of the part, this is likely a normal consequence

of the quench and tempering process. In short, the microstructure of the two nozzle pieces are similar as shown in Figure A7, consisting primarily of very fine structure that cannot be resolved with optical light microscopy. This type of microstructure is expected for a quench and tempered martensitic steel.

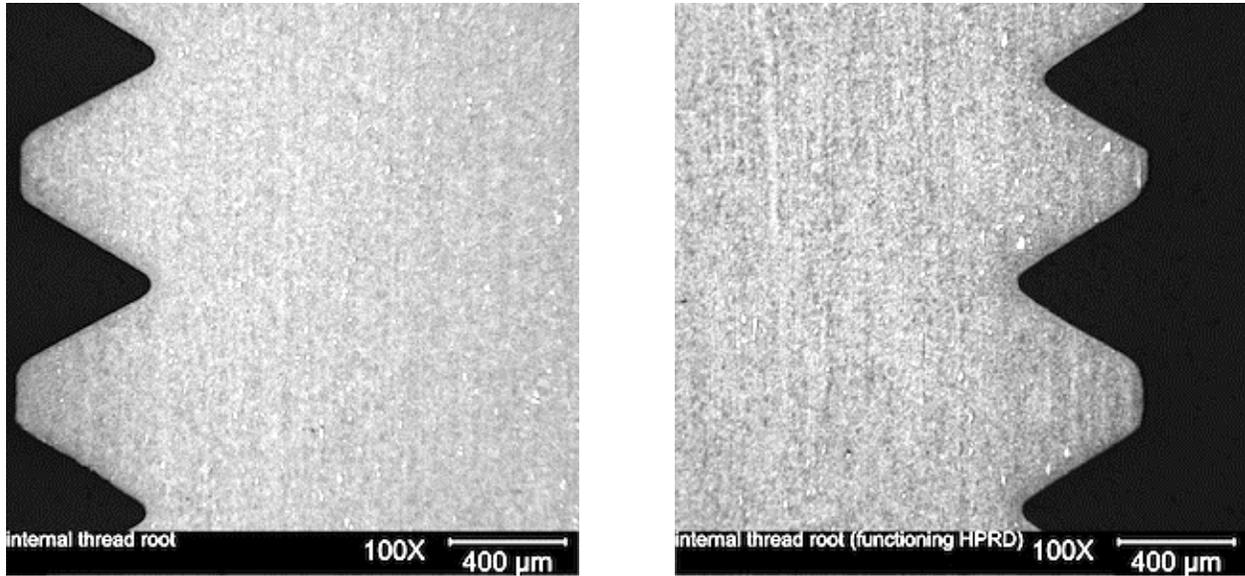


Figure A6. Light microscopy images of internal thread root of (a) the failed nozzle and (b) the functioning nozzle. Cracking at the root of threads (and other machined features) was not observed.

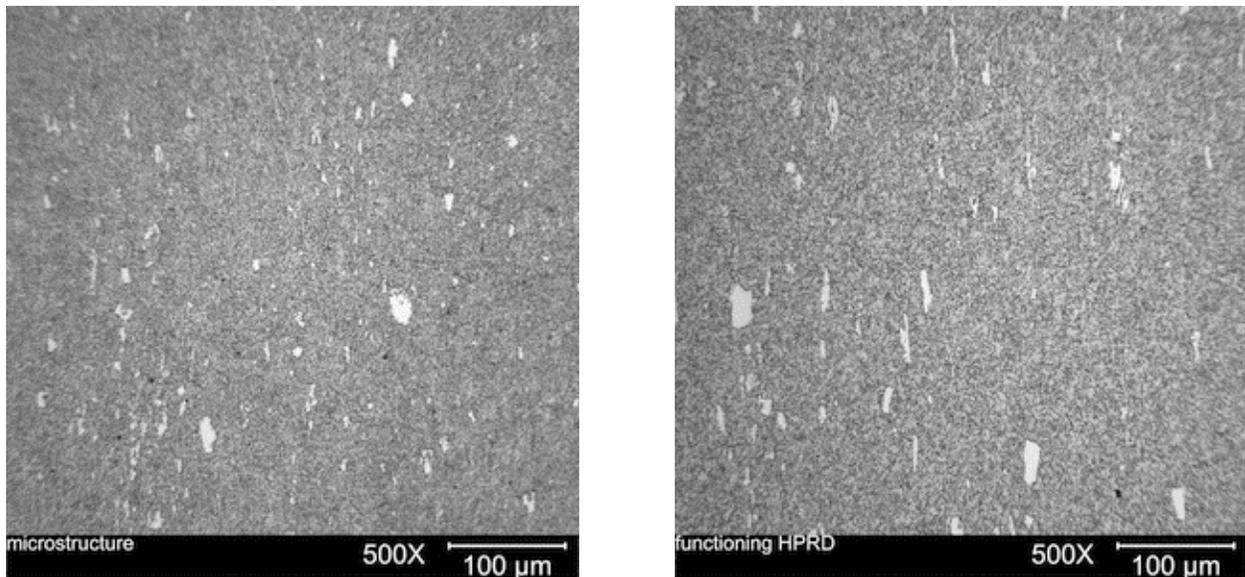


Figure A7. Microstructure of (a) the failed nozzle and (b) the functioning nozzle. This microstructure is consistent with that of a quench and tempered martensitic steel.

A.5.5. Fractography

The parts in the as-received condition were extremely dirty. The lack of cleanliness obscured fracture surface of the as-received part labeled A1 and little could be determined from this examination (Figure A8). After sectioning to produce B1, the mating fracture surface (A2) was cleaned ultrasonically for a short duration prior to observation; this removed contamination from the cutting fluid during sectioning, as well as contamination from general handling. The cleaning operation was minimized to prevent damage to the fracture surface. While examination of this surface revealed characteristics of the true fracture surface, many portions of the surface remained obscured by dirt and debris. Further cleaning was not attempted.

Examination of A2 did reveal a fracture surface with very fine structure, representative of the very fine microstructure. Classic brittle fracture was not observed, likely due to the fine microstructure. High-resolution images (Figure A9) suggest fine facets at submicron length scales. While the analysis is not definitive in this regard, these structures appear to be associated with boundary separation, a fracture feature often observed as a consequence of environmental-assisted cracking.

A.6. Conclusions

- Type 440C martensitic stainless steel is a poor choice of structural material for hydrogen service. Comparison with literature data (Figure A3) demonstrates that generally metals with yield strength >1000 MPa are severely embrittled by exposure to gaseous hydrogen, the yields strength of type 440C is significantly greater.
- Fractography suggests environmental-assisted fracture.
- Possible contributing factors:
 - The hardness of the failed nozzle was substantially higher than the hardness of the functioning nozzle. The discrepancy in measured hardness suggests that the failed nozzle was not properly heat treated, since the hardness of the failed nozzle is substantially greater than another nozzle from the same installation.
 - External damage was observed on the failed nozzle, but not on the functioning nozzle.

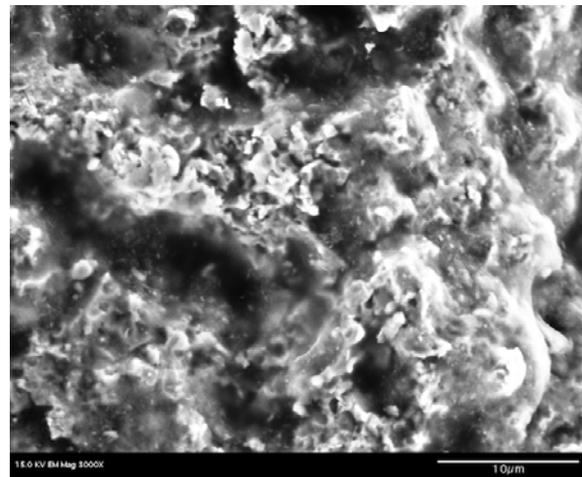
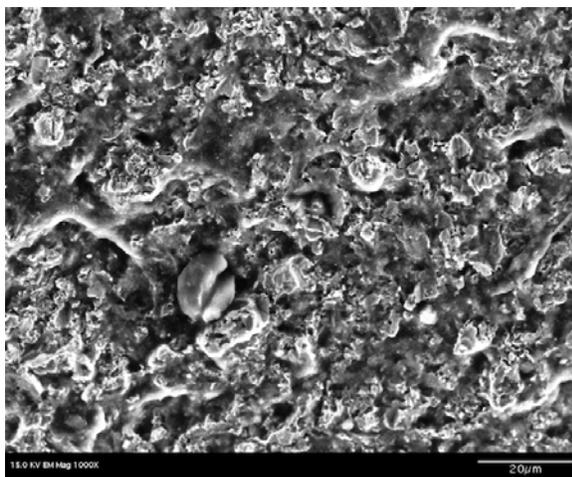


Figure A8. Fracture surface of A1 showing dirt and debris on the surface.

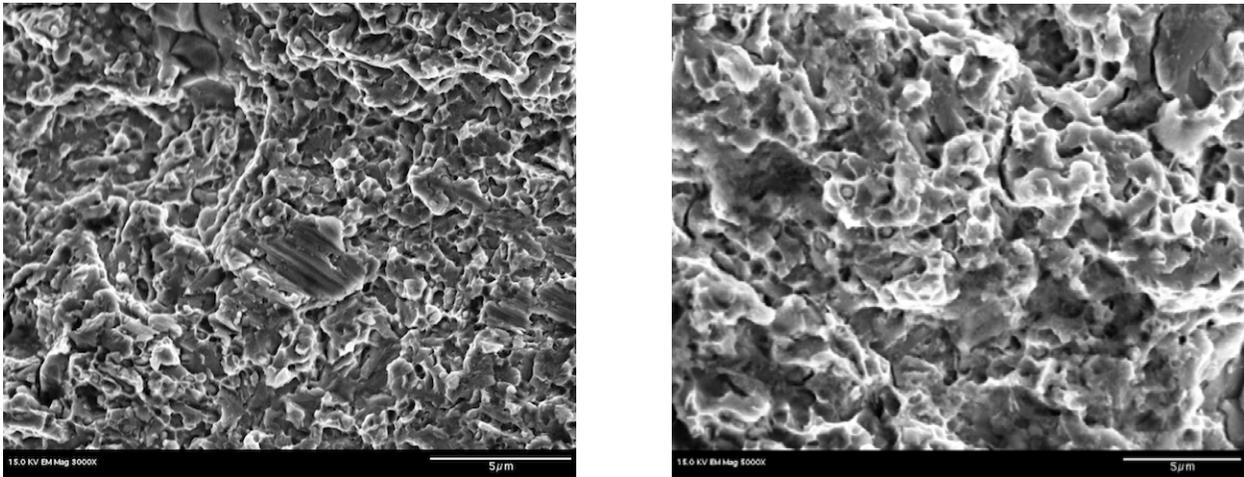


Figure A9. Fracture surface of A2 after light cleaning. These two images from distinct areas of the fracture surface show flat fracture features representative of low ductility.

A.7. Test Protocol

A.7.1. Phase I: Non-Destructive Examination

1. Examine (visually) and photo-document the components of the failed pressure relief valve and the functioning pressure relief valve. The functioning pressure relief valve will be disassembled per the manufacturers guidance prior to documentation of the components.
2. Measure the basic dimensions of the components marked A thru D (Figure A2) with calipers or similar calibrated tools; the components from the functioning pressure relief valve and the failed pressure relief valve shall be similarly documented. All of the dimensions per the print will not be evaluated.
3. Examine the components marked A thru D (Figure A2) with a stereomicroscope and photo document as necessary; the components from the functioning pressure relief valve and the failed pressure relief valve shall be similarly documented.
4. Examine the fracture surface of the smaller of the two pieces of the nozzle body (A1) with scanning electron microscopy (SEM) and acquire images as appropriate. The fracture surface shall not be cleaned, coated or otherwise altered in any manner.
5. Examine selected areas of the fracture surface of A1 with energy dispersive spectroscopy (EDS) for qualitative elemental analysis and record as appropriate.
6. Store components in separate containers to preserve their integrity and identity. Set aside with the exception of component B.

A.7.2. Phase II: Destructive Examination

A.7.2.1. Failed pressure relief valve

7. Cut the inlet base (B) of the failed pressure relief valve approximately along the line shown in Figure A10 with electric discharge machining (EDM) or other suitable cutting method. Immediately rinse the fracture surface of the nozzle body with alcohol and dry. Identify the two pieces as B1 (containing the fracture surface) and B2 (containing the inlet threads). Store B2 in accordance with the other components.
9. Examine the fracture surface from B1 with SEM and take images as appropriate. The fracture surface shall not be coated or otherwise altered in any manner.
10. Examine selected areas of the fracture surface of B1 with EDS for qualitative elemental analysis and record as appropriate.
11. Cut the piece containing the fractured nozzle body (B1) approximately along the line shown in Figure A11 using an appropriate precision cutting method (e.g., EDM or diamond wafering blade). If coolant is used with the cut off saw, immediately rinse the fracture surface of the valve seat with alcohol and dry. This cutting operation should result in six pieces: two of the nozzle body, two of the soft seat and two of the inlet base. Identify the two nozzle body pieces as A2-1 and A2-2, the two up-stream pieces (if they separate from the nozzle body) as A2-3 and A2-4 and the two inlet base pieces as B1-1 and B1-2. Store A2-3, A2-4, B1-1 and B1-2 in accordance with the other components.
12. Examine pieces A2-1 and A2-2 with the stereomicroscope and photo document as necessary.
13. Select either piece A2-1 or A2-2 for wet quantitative chemical analysis per ASTM Standard E350, or equivalent. The chemical analysis should include LECO combustion technique for carbon content and LECO RH-404 hydrogen analyzer per ASTM E1447, for dissolved residual hydrogen content. The selected piece will be destroyed during these compositional analyses.
14. Mount the remaining piece (either A2-1 or A2-2) in suitable resin or mounting compound such that the thread root and fracture surface are shown in cross section. Grind and polish using standard metallographic techniques.
15. Examine the mounted sample with the optical microscope and document with micrographs as appropriate.
16. Etch the mount with an etchant suitable for martensitic stainless steels (e.g., Viella's etchant) and re-examine with the optical microscope. Document with micrographs as appropriate.
17. Perform microhardness measurements on the etched surface at selected locations using a calibrated diamond pyramid hardness tester and, if appropriate, by Rockwell Hardness Scale C. Record as appropriate.
18. Store the mounted sample with other components with attention to preserving the polished surface.

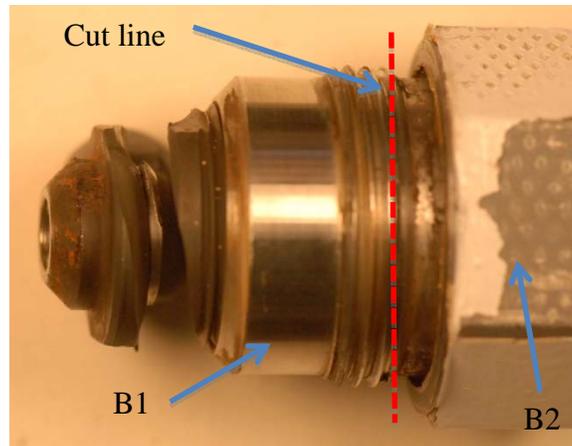


Figure A10. Approximate location of cut line to separate nozzle subassembly from inlet base.

A.7.2.2. Functioning pressure relief valve

19. Remove the nozzle subassembly from the functioning pressure relief valve. Identify the nozzle assembly as part A. If subassembly cannot be easily removed, proceed to step 21 and section following step 11.
20. Examine the nozzle subassembly with the stereomicroscope and photo document as necessary.
21. Cut the nozzle body along a line containing the axis of the part using an appropriate precision cutting method (e.g., EDM or diamond wafering blade). Identify the two pieces as A-1 and A-2.
22. Select either piece A-1 or A-2 for wet quantitative chemical analysis per ASTM Standard E350, or equivalent. The chemical analysis should include LECO combustion technique for carbon content and LECO RH-404 hydrogen analyzer per ASTM E1447, for dissolved residual hydrogen content. The selected piece will be destroyed during these compositional analyses.
23. Mount the remaining piece (either A-1 or A-2) in suitable resin or mounting compound so that the thread root and profile of the part are shown in cross section. Grind and polish using standard metallographic techniques.

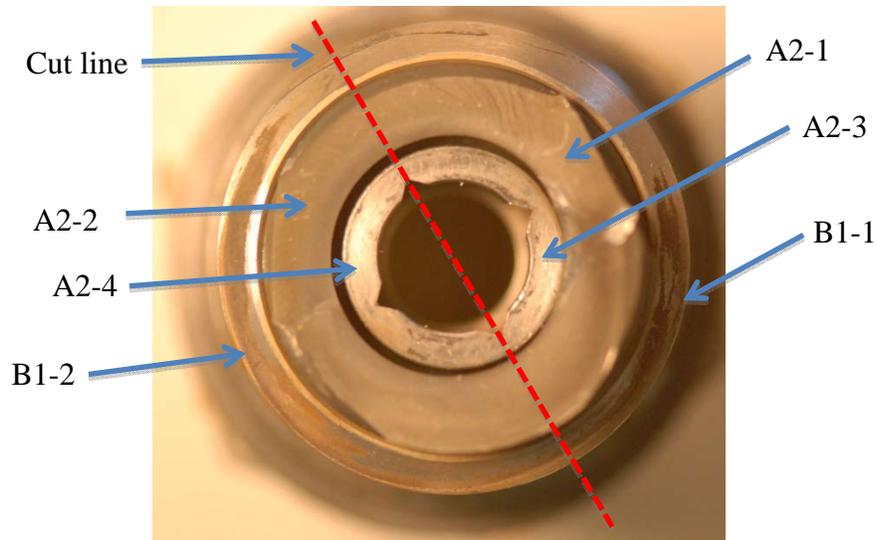


Figure A11. Approximate location of sectioning for metallographic profile.

24. Examine the mounted sample with the optical microscope and document with micrographs as appropriate.
25. Etch the mount with an etchant suitable for martensitic stainless steels and re-examine with the optical microscope. Document with micrographs as appropriate.
26. Perform microhardness measurements on the etched surface at selected locations using a calibrated diamond pyramid hardness tester and, if appropriate, by Rockwell Hardness Scale C. Record as appropriate.
27. Store the mounted sample with other components with attention to preserving the polished surface.

A.7.2.3. Review and Archive

28. Draft report of metallurgical investigation and acquire review and approval for distribution (from testing laboratory and Investigative Representatives).
29. Review draft report with Investigative Representatives at testing laboratory. Investigative Representatives may request any of the microscopy steps be repeated and witnessed. Sample preparation steps (polishing, etching, etc) will be repeated and witnessed at the discretion of the testing laboratory. Some steps require destroying or loss of materials and cannot be repeated.
30. Finalize report and determine distribution.
31. Upon completion of this protocol, all components and data will be stored at the testing laboratory.

A.8. References

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A.9. Biographical Information

Mr. Harris obtained his master's degree in Mechanical Engineering from the University of Washington in 2007 and holds a BS in Mechanical Engineering. Currently Mr. Harris is a Senior Project Engineer at Sandia National Laboratories responsible for project management of the Hydrogen Safety, Codes and Standards portion of Sandia's Hydrogen Energy Program. Mr. Harris recently joined Sandia National Laboratories from Nuvera Fuel Cells where he served in a variety of roles including Safety and Product Compliance Manager. Mr. Harris has presented many times on the topics of hydrogen safety, codes and standards to a variety of audiences including informal training for local and regional fire service personnel. Mr. Harris has served or currently serves on multiple code and standard development committees through NFPA, CSA, IEC and ISO. Mr. Harris also serves on the US DOE Hydrogen Safety Panel. In addition, Mr. Harris is a certified firefighter/EMT including participation in the US DOE hydrogen first responder operations level training program.

Dr. Chris San Marchi obtained a PhD in Materials Science from MIT in 1997 and holds BS degrees in Mechanical and Aerospace Engineering as well as in Chemistry. Currently Dr. San Marchi is a Principal Member of the Technical Staff at Sandia National Laboratories in the Hydrogen and Metallurgy Science Department. Dr. San Marchi has extensively published in the area of hydrogen-assisted fracture, including authoring the online Technical Reference for Hydrogen Compatibility of Materials and several contributions to distinguished texts. Dr. San Marchi contributes to several code development activities in the area of hydrogen infrastructure and owns responsibility for stainless steels and forging for mission critical Sandia products.

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