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Continuing the Evaluation of All-Metal Valves for Use in a Tritium Environment

L. R. Houk

A. N. Payton

September 2018

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EXECUTIVE SUMMARY

It is desired in tritium gas processing systems to minimize the use of polymer components due to their degradation from tritium exposure (beta decay). One source of polymers in tritium processes are valve components. An all-metal diaphragm valve with no plastic wetting components could be used in certain tritium applications to reduce organic materials in the tritium process.

The Ham-Let Group has been identified as a manufacturer that makes all-metal diaphragm valves. Twelve (12) 3LE Series Ham-Let all metal diaphragm valves, with a stated 100,000 cycle life, were procured for characterization and evaluation. Valves were cycled until failure or up to 750,000 cycles in either nitrogen, vacuum, or a combination of nitrogen/vacuum on either side of the valve. Valve failure was defined when the leak rate exceeded $4.0x10^{-9}$ STD cc He/sec. Valve cycle testing followed the ASTM F1373-93, "*Standard Test Method for Determination of Cycle Life of Automatic Valves for Gas Distribution System Components*."

Seven valves were cycled at ambient temperature, with a nitrogen process gas, up to 750,000 cycles while five valves where cycled at 105°C, with a hydrogen process gas, up to 125,00 cycles. One nitrogen cycled valve failed at 20,000 cycles due to plastic debris embedded into the diaphragm. Two other nitrogen cycled valves failed the leak rate criteria, but then passed leak testing upon further cycling leading to the speculation particulates were present and temporarily altered valve performance. Two hydrogen cycled valves had similar valve failures-valve recovery test histories: even after installation of filters in the test manifold to mitigate particulate contamination.

Two nitrogen cycled valves failed the body leak rate criteria after 500,000 or more cycles, but no direct causality could be assigned to the failure mechanism. Both valves had vacuum on the outlet of the valve during cycling (one had nitrogen, the other vacuum, on the valve inlet), but "twins" of the failed valves (valves cycled under the same test conditions) did not fail any of the leak tests even after 750,000 cycles so no definite conclusions could be made about absolute valve cycle limits.

Two hydrogen-cycled failed valves both passed the body leak rate criteria after 100,000 cycles or more indicating the failure mechanism to be the sealing of the diaphragm to the valve body. Both valves had hydrogen on the outlet of the valve during cycling (one hydrogen, the other vacuum, on the valve inlet), but one "twin" of one failed valve continued to pass leak rate testing, even after 125,000 cycles. One failed valve diaphragm which was in contact with the process gas had noticeable surface "modifications", but the composition of the modified surface and the impact valve sealing is still unknown. It is not clear if cycling the valves in hydrogen, at elevated temperature, or use of hydrogen gas with 500 ppm impurities inhibited sealing of the diaphragm with the valve body.

The valves tested met or exceeded the manufacture stated cycle life. Additional technical questions for tritium usage include the permeation rate of tritium through the diaphragm during process operations and the impact of He-3 on the mechanical properties of the diaphragm. If permeation rates through the diaphragm are acceptable and the impact of He-3 does not shorten the valve life to less than the currently used polymer-tipped bellow seal valves, the all metal diaphragm valves may be a suitable replacement for some polymeric tipped valves. Tritium leakage from valves with diaphragm failures (e.g. valves which fail the body leak rate criteria) after very high valve cycling (greater than 100,000 cycles) may limit the use of these valve to low tritium content gas or valves contained in secondary confinement such as gloveboxes.

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LIST OF ABBREVIATIONS

D	Deuterium
EDS	Energy-dispersive X-ray spectroscopy
H	Hydrogen (protium)
HV	Hydrogen Valve
IV	Isolation Valve
Mo-99	Molybdenum-99
psi	pounds per square inch – a unit of pressure
psig	pounds per square inch gauge – a unit of pressure
PTFE	Polytetrafluoroethylene or Teflon
SEM	Scanning Electron Microscope
SRNL	Savannah River National Laboratory
STD cc He /sec	One cubic centimeter of helium gas flow per second at 760 torr and 25˚C
T	Tritium
TV	Test Valve
UHMW-PE	Ultra-High-Molecular-Weight Polyethylene

1.0 Introduction

Tritium is a radioactive isotope of hydrogen that decays to helium-3. The conversion of the neutron to a proton in the nucleus gives off beta radiation [1]. Tritium gas reacts with and degrades polymer components. Elimination of polymers from tritium exposed valve components could result in a longer valve service life. Additional benefits, other than cost avoidances related to less frequent maintenance and replacement, includes decreased byproduct impurity gas formation and particulate generation in the process system.

Polymer components in valves can fail when exposed to tritium. Some valves contain polymer components wetted/in contact with the process fluid. Polytetrafluoroethylene (PTFE or Teflon), UHMW-PE (Ultra High Molecular Weight Polyethylene) or Vespel® (high performance polyimide-based plastics manufactured by Dupont) are commonly used polymers found in valves. Vespel® is generally preferred over PTFE for tritium applications [2]. PTFE is usually avoided in tritium applications because the fluoro-groups in PTFE can react with the tritium gas and create hydrofluoric acid, QF, where Q represents any of the hydrogen isotopes protium (H), deuterium (D), or tritium (T). Tritiated hydrofluoric acid is especially undesirable for its potential to corrode stainless steel.

Tritium also affects polymer material properties. Some polymers, such as PTFE and UHMW-PE, change color when exposed to tritium for several months [3] [4] [5]. Polymer embrittlement and fracture into smaller pieces which may travel throughout a tritium process system and clog filters and other equipment [6] is more of a concern than color change. As particles are move through the system, the chance for leaking valves increases due to particles altering the gas sealing surface.

Using tritium valve technical guidelines during the requisitions of valves can prevent some of these issues. Several manufacturers offer valves that meet the recommended tritium valve technical guidelines [2] – either all-metal bellows-type valves or diaphragm valves which minimize the use of polymers that are detrimental to tritium gas processing systems. The specific design parameters for the valve location must be considered in the selection of the appropriate valve type. Often, the confinement characteristics of a metal bellows valve is desirable, and either a hardened polymer or metal components (e.g. copper) may be used, depending on the chemical composition of the gas process flow stream. In other situations, an all-metal diaphragm valve may be desirable to meet the design performance characteristics.

A study of commercially available all-metal diaphragm valves was initiated in 2016 to identify alternatives to metal bellows valves. In many cases, metal bellows valves require a large actuator to meet leak rate criteria. The all-metal diaphragm valve with actuator identified in this evaluation is smaller than the corresponding metal bellows valve with actuator. The reliability and performance characteristics of the all-metal diaphragm valve have not been previously studied for tritium service.

1.1 All-Metal Diaphragm Valve Overview

Ham-Let Group manufactures a diaphragm valve in which all wetted components are made of metal, meaning any fluid passing through the valve will only "wet" or touch metal. This all-metal diaphragm valve could be used in the tritium gas process if performance characteristics can be validated. Figure 1-1 shows the selected diaphragm test valve, model number 3LES4C-FV-U [7]. This ultra-clean valve boasts a small footprint, measuring less than 4" in width and height, which is ideal for applications in gloveboxes, Figure 1-2. The manufacture stated maximum operating pressure is 150 psi with a working temperature range of -10 to 150˚C. The manufacturer supplied data sheet [7] states the only wetted components are the valve body and the diaphragms. Though the option to include limit switches is available, these tests did not utilize limit switches on the valve.

3LE SERIES

COMPACT METAL SEAT MODEL

Metal Diaphragm Valves

The highest-ranking grade of compact models from the Ultra-Clean Valve Series are made according to UHP specifications. It is the ultimate in metallic diaphragm-operated valves with resins completely removed from their gas-contact areas. Their minimized valve internal volumes also best recommended them for use in liquid source supply applications.

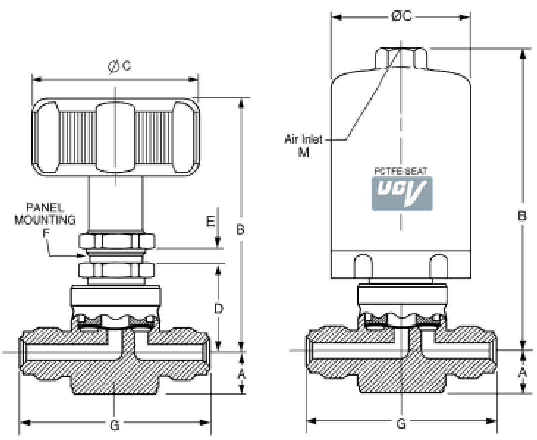
- Compact designs for minimum footprint.
- High-speed replacment of fluids in a gas or liquid state.
- Electropolished surfaces.

For details, please contact one of our field representatives.

ULTRA CLEAN VALVES

STANDARD CONFIGURATION DIMENSIONS

Part Number/ep	Size	End Connection	A	B	C	D	E	F	G	K	M
3LES2R-BV-U	1/8	Male HTC®	8	(51)	30	23	(4)	15	41	15	
3LES4R-W-U	1/4	Extended ButtWeld	11	(52)	30	24.5	(4)	17	47	17	
3LES4C-BW-U	1/4	Short ButtWeld	11	(86.2)	32	24.5	(4)	17	44.4	17	Rc1/8
3LES4C-FV-U	1/4	Swivel Female HTC®	11	(86.2)	32				66	17	Rc1/8



SPECIFICATIONS

Size	Pressure	Temp.	Cv	Leak Rates Inboard	Leak Rates Across Seat
1/8	1MPa (150 psi)	-10 to 150°c	0.05	3×10^{-12} pa•m³/sec Helium	1×10^{-9} pa•m³/sec Helium
1/4			0.1		

STRUCTURE

	Parts	Material
1	Body	Stainless steel, 316L Var or Vim/Var[1]
2	Diaphragm	Co-Cr-Ni Alloy
3	Act. Button Set	304 Stainless Steel
4	Act. Button Holder	Stainless Steel, ASTM 630 H900
5	Actuation Device	Aluminum

(1) Per SEMI F20-0305

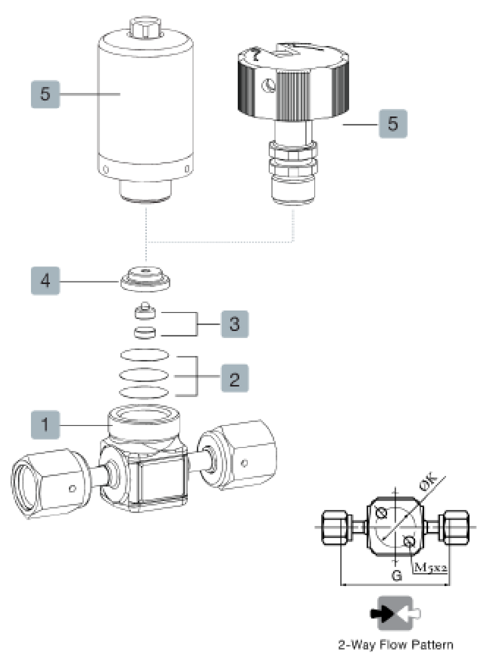


Figure 1-1. Product Description of an All-Metal Diaphragm Valve from Ham-Let [7]

Figure 1-2. Pictures of As-Received All-Metal Diaphragm Valve

A typical bellows valve, Figure 1-3a, uses a stem tip pressed into the valve body to stop the gas flow: retraction of the valve tip from the valve body "opens" the valve allowing gas to flow. The Ham-Let valve diaphragm in the down position, indicated as the dark wave in Figure 1-3b, shows the valve in the closed position sealing off gas flow. When the valve is opened, the actuator is lifted, and the diaphragm rises from the valve body allowing for the gas to pass through the valve body.

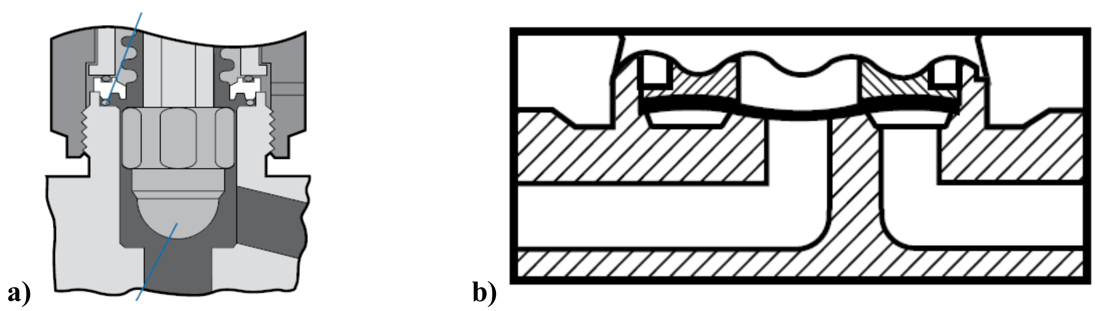


Figure 1-3. a) Typical Bellows Valve, with a Stem Tip [8] b) Typical Diaphragm Valve [7]

A photograph of a cut away valve is shown in Figure 1-4. Disassembly of the Ham-Let valve reveals the valve diaphragm consists of three diaphragms made from two different cobalt alloys. The wetted diaphragm is made from SPRON510 while the two non-wetted diaphragms are made from Elgiloy. On top of the diaphragms are the actuator components, which consists of an actuator button set and a button holder (also see Figure 1-1). The button set has a polyimide plastic component in contact with the top diaphragm and a stainless-steel button over the plastic. The actuator button set goes inside the actuator button holder which contacts the actuator for opening and closing the valve.

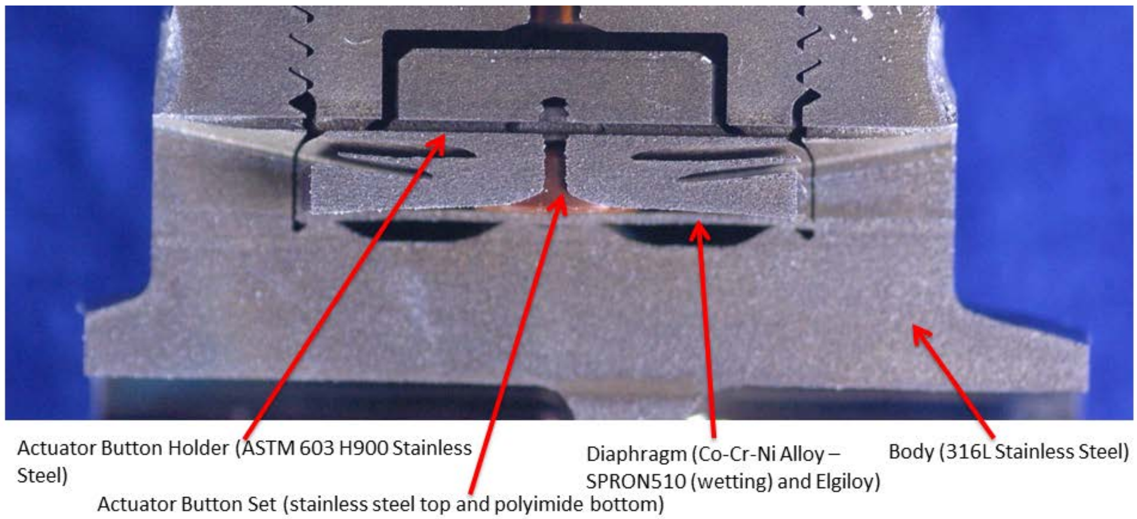


Figure 1-4. Detailed Cross Sectional Image of Valve Body with Main Parts Labeled and Materials Identified

1.2 Valve Testing Scope

Initial evaluation of the all-metal diaphragm valve has been reported previously [9]. Characterization included pressure testing of valves, initial materials characterization, and preliminary nitrogen cycle test results. The maximum acceptable leak rate was defined as 4.0×10^{-9} STD cc He/sec based on typical leak rates from vacuum component manufacturers. An initial, baseline leak test was performed on all valves. All but one valve passed the initial leak test. The failed valve leaked through the connection from the body to the actuator. Seven valves were then cycled in a nitrogen and/or vacuum environment. The manufacturer's stated cycle life was stated as 100,000 cycles. This work summarizes cycle test results of the Ham-Let diaphragm valves in nitrogen and hydrogen along with characterization of valve failure(s).

2.0 Experimental Configuration and Results

One valve cycle was counted for each time the diaphragm was opened and then returned to its seated/closed position. The tests were conducted to evaluate the sealing performance of the valve seat and diaphragm and not evaluate the cycle life of the valve actuator. After the valves completed a specified number of cycles, they were removed from the manifold for testing in accordance with ASME Section V, Article 10, helium (He) seat leak testing (internal leak check past the valve seat or through the closure member when the valve is closed) and body testing (external leak check to evaluate leakage from pressure inside the valve out to the surrounding atmosphere) using a calibrated helium mass spectrometer. During leak tests, the helium pressure was maintained at 150 psig ± 5 psig. A passing leak rate was defined as 4.00×10^{-9} STD cc He/sec or less. Shell leak checks were performed for 3 min. After leak checking, the valves were reinstalled onto the manifold and cycling recommenced.

2.1 Diaphragm Valves Cycled in Nitrogen

Previously, the diaphragm valves were cycle in nitrogen up to 200,000 cycles, which greatly exceeded the manufacturer's valve life expectancy of 100,000 cycles [9]. For nitrogen cycling, the valve cycling rate was every 4 to 5 seconds (for a rate of 12 cycles per minute). In summary, only one of the seven valves tested (TV01) failed at the first leak-test interval of 20,000 cycles and had nitrogen on both the inlet and the outlet. Two other valves (TV02 and TV05) passed initial cycling tests, later failed leak rate tests after further cycling, but then passed the leak rate criteria after installation of additional filters in the test manifold. Individual valve leak testing was performed every 50,000, 100,000 and finally 250,000 cycles instead of every 10,000 cycles for the extended cycle testing.

2.1.1 Experimental Set-up for Nitrogen Cycling

The full experimental configuration of the nitrogen cycling manifold was discussed in a previous report [9]. The test system schematic is shown in Figure 2-1, and a photograph of the test system in Figure 2-2. Four different valve cycling conditions were tested: nitrogen on the inlet and outlet; nitrogen on the inlet and vacuum on the outlet; vacuum on the inlet and nitrogen on the outlet; and vacuum on both the inlet and the outlet. Each of these conditions had two valves except for the vacuum on the inlet and nitrogen on the outlet, which just had one valve. The valve testing conditions were at ambient temperatures and 45 psig nitrogen.

After failure of valves TV02 and TV05, determined to be caused by particulates, additional filters were installed on the test manifold. A 0.003 µm filter was installed on the gas inlet line to remove particulates from the incoming gas and two additional 0.5 µm filters were installed downstream of isolation valves IV15 and IV18 to capture Teflon particulates which may originate from these valves.

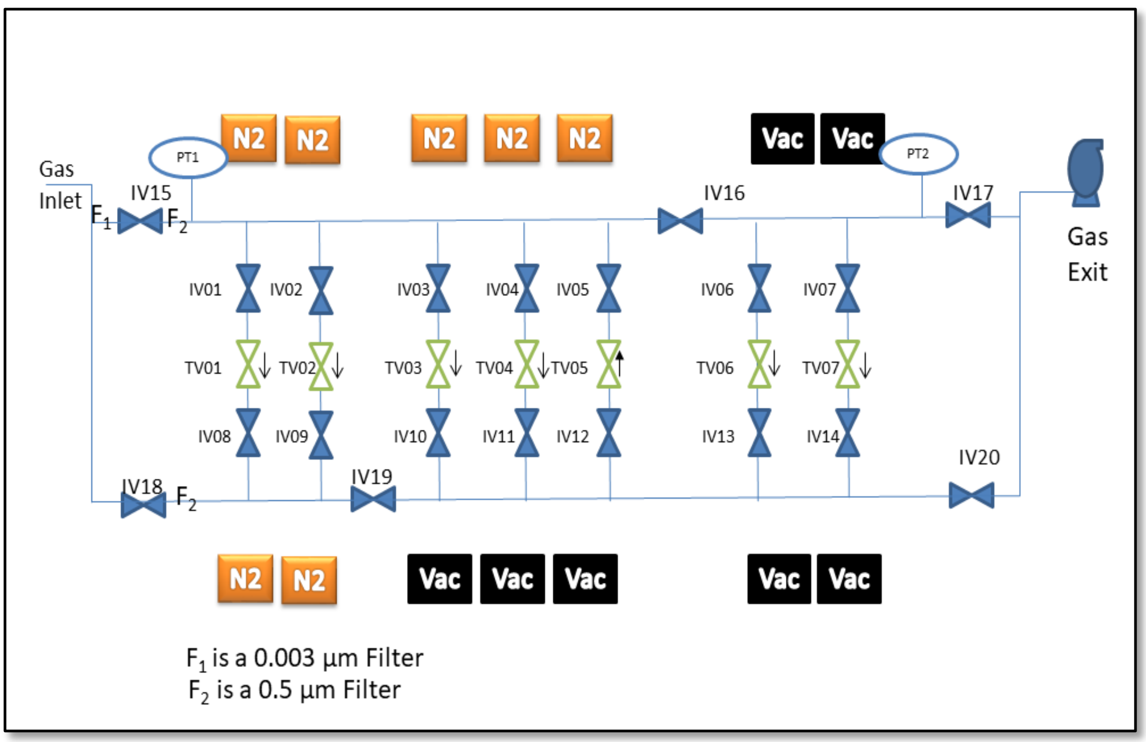


Figure 2-1. Diagram of Valve Testing Manifold for Nitrogen Gas Environments

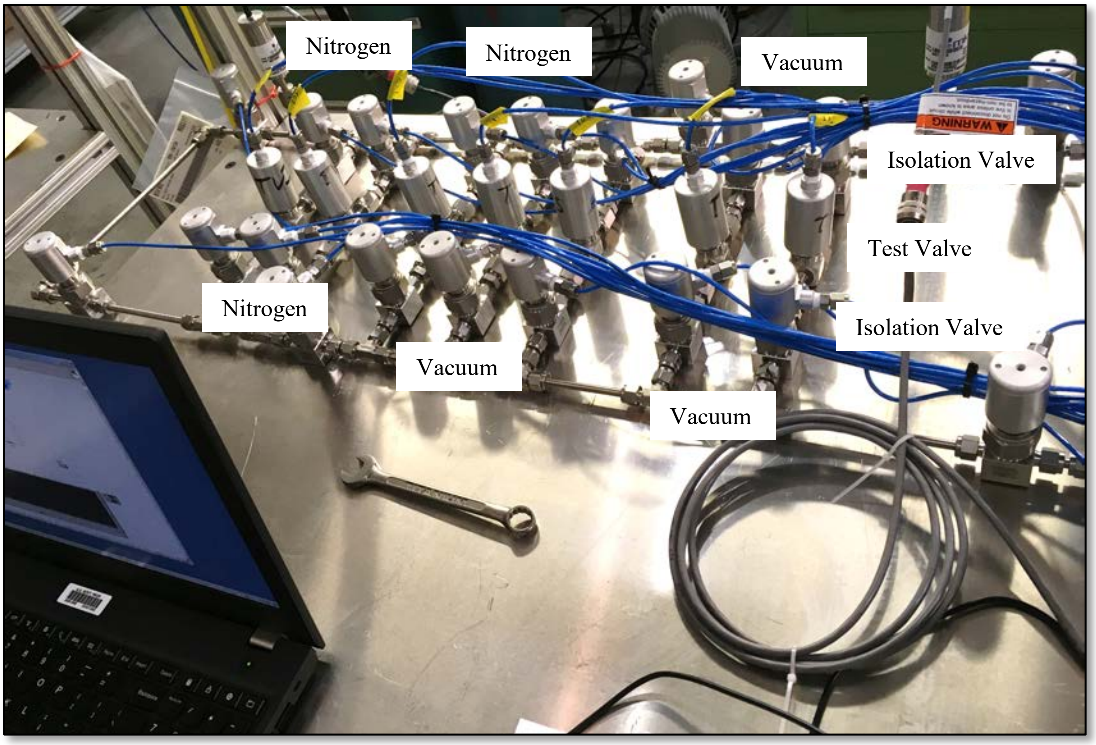


Figure 2-2. Photograph of Valve Testing Manifold Set-Up for Nitrogen (Before Filters were Installed)

2.1.2 Nitrogen Experimental Cycling Results

A summary of valve leak test results is provided in Table 2-1. Valves were cycled until failure or until they attained a cumulative 750,000 cycles. A body leak rate test was used for the first 40,000 cycles instead of a valve outlet seat leak test. After 40,000 cycles, a body leak rate test was only conducted after the valve had failed. The individual valve leak rate tests were performed every 50,000, 100,000 and finally 250,000 cycles instead of every 10,000 cycles for the extended cycle testing.

After 50,000 cycles, the valves continued to pass the leak rate tests until reaching 400,000 cycles as shown in Figure 2-3 and Figure 2-4. After 400,000 cycles, TV04 failed to pass the leak test and had a leak rate greater than 1 x 10^{-4} STD cc He/sec – the upper range of the He mass spectrometer leak detector. Valves TV04 and TV05 had nitrogen on the valve inlet and vacuum on the outlet during cycle testing, but TV05 did not fail leak tests after the addition of filters to the test manifold.

TV07 was the only other valve that failed and had vacuum on the inlet and outlet of the valve. This valve failed after 500,000 cycles with a leak rate outside the range of the He mass spectrometer leak detector. The twin for this valve, TV06, passed all leak tests.

Table 2-1. Leak Rates of Inlet and Outlet Seat for Nitrogen-Cycled Valves

Test Valve Figure 2-2	TV01 N_2/N_2		TV02 N_2/N_2		TV03 N_2/Vac		TV04 N_2/Vac		TV05 Vac/N_2		TV06 Vac/Vac		TV07 Vac/Vac	
# of Cycles	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Leak Inlet[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]	Seat Inlet Leak[1]	†Body Leak[1] §Seat Outlet Leak [1]
0	< 8.4 x 10^{-10}	§< 8.4 x 10^{-10}	< 8.3 x 10^{-10}	†< 8.3 x 10^{-10}	< 8.8 x 10^{-10}	†< 8.8 x 10^{-10}	< 8.8 x 10^{-10}	†< 8.8 x 10^{-10}	< 8.7 x 10^{-10}	†< 8.7 x 10^{-10}	< 8.8 x 10^{-10}	†< 8.8 x 10^{-10}	< 9.0 x 10^{-10}	†< 9.0 x 10^{-10}
20,000	1.2 x 10^{-4}	†< 1.1 x 10^{-9}	< 1.2 x 10^{-9}	†< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	†< 1.2 x 10^{-9}	1.7 x 10^{-9}	†1.4 x 10^{-8}	6.3 x 10^{-9}	†< 9.5 x 10^{-10}	< 9.5 x 10^{-10}	†< 9.5 x 10^{-10}	1.4 x 10^{-9}	†< 9.4 x 10^{-10}
40,000	9.2 x 10^{-4}	†< 8.4 x 10^{-10}	< 9.0 x 10^{-10}	†< 9.0 x 10^{-10}	< 8.6 x 10^{-10}	†< 8.6 x 10^{-10}	< 1.2 x 10^{-9}	†< 1.2 x 10^{-9}	< 1.0 x 10^{-09}	†< 1.0 x 10^{-09}	< 9.4 x 10^{-10}	†< 9.4 x 10^{-10}	< 1.0 x 10^{-9}	†< 1.0 x 10^{-9}
50,000	X	§X	8.6 x 10^{-4}	§1.6 x 10^{-9}	< 9.8 x 10^{-10}	§1.3 x 10^{-9}	1.7 x 10^{-9}	§2.6 x 10^{-9}	6.1 x 10^{-5}	§1.6 x 10^{-9}	1.5 x 10^{-9}	§2.3 x 10^{-9}	1.1 x 10^{-9}	§1.6 x 10^{-9}
60,000	NT	NT	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.2 x 10^{-9}	§ 1.6 x 10^{-9}	< 1.2 x 10^{-9}	§1.6 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}
70,000	X	§X	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}
80,000	NT	NT	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}
90,000	NT	NT	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}
100,000	NT	NT	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}
150,000	NC	NC	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}
200,000	NC	NC	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}
250,000	NC	NC	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}	< 1.3 x 10^{-9}	§< 1.3 x 10^{-9}
300,000	NC	NC	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 9.9 x 10^{-10}	§< 9.9 x 10^{-10}
350,000	NC	NC	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 9.9 x 10^{-10}	§< 9.9 x 10^{-10}	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}
400,000	NC	NC	< 9.2 x 10^{-10}	§< 9.2 x 10^{-10}	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.2 x 10^{-9}	§< 1.2 x 10^{-9}	< 1.1 x 10^{-9}	§< 1.1 x 10^{-9}	< 1.4 x 10^{-9}	§< 1.4 x 10^{-9}	< 9.5 x 10^{-10}	§< 9.5 x 10^{-10}
500,000	NC	NC	< 1.4 x 10^{-09}	§< 1.4 x 10^{-09}	< 1.4 x 10^{-09}	§< 1.4 x 10^{-09}	X	X	< 1.0 x 10^{-9}	§< 1.0 x 10^{-9}	< 1.4 x 10^{-9}	§< 1.4 x 10^{-9}	< 1.4 x 10^{-9}	§< 1.4 x 10^{-9}
750,000	NC	NC	< 1.4 x 10^{-09}	§< 1.4 x 10^{-09}	< 9.0 x 10^{-10}	§< 9.0 x 10^{-10}	X	X	< 7.6 x 10^{-10}	§< 7.6 x 10^{-10}	< 8.2 x 10^{-10}	§< 8.2 x 10^{-10}	X	X

Notes:

A passing leak rate is defined as 4.00 x 10^{-9} STD cc He/sec or less.

[1] Leak Rates in STD cc He/sec

X Denotes the Leak Rate is a Higher than Detectable by the Helium Mass Spectrometer Detection

† Denotes Body Leak test was used

§ Denotes Seat Outlet Leak was used

NT Denotes Valve Not Tested

NC Denotes Valve Not Cycled

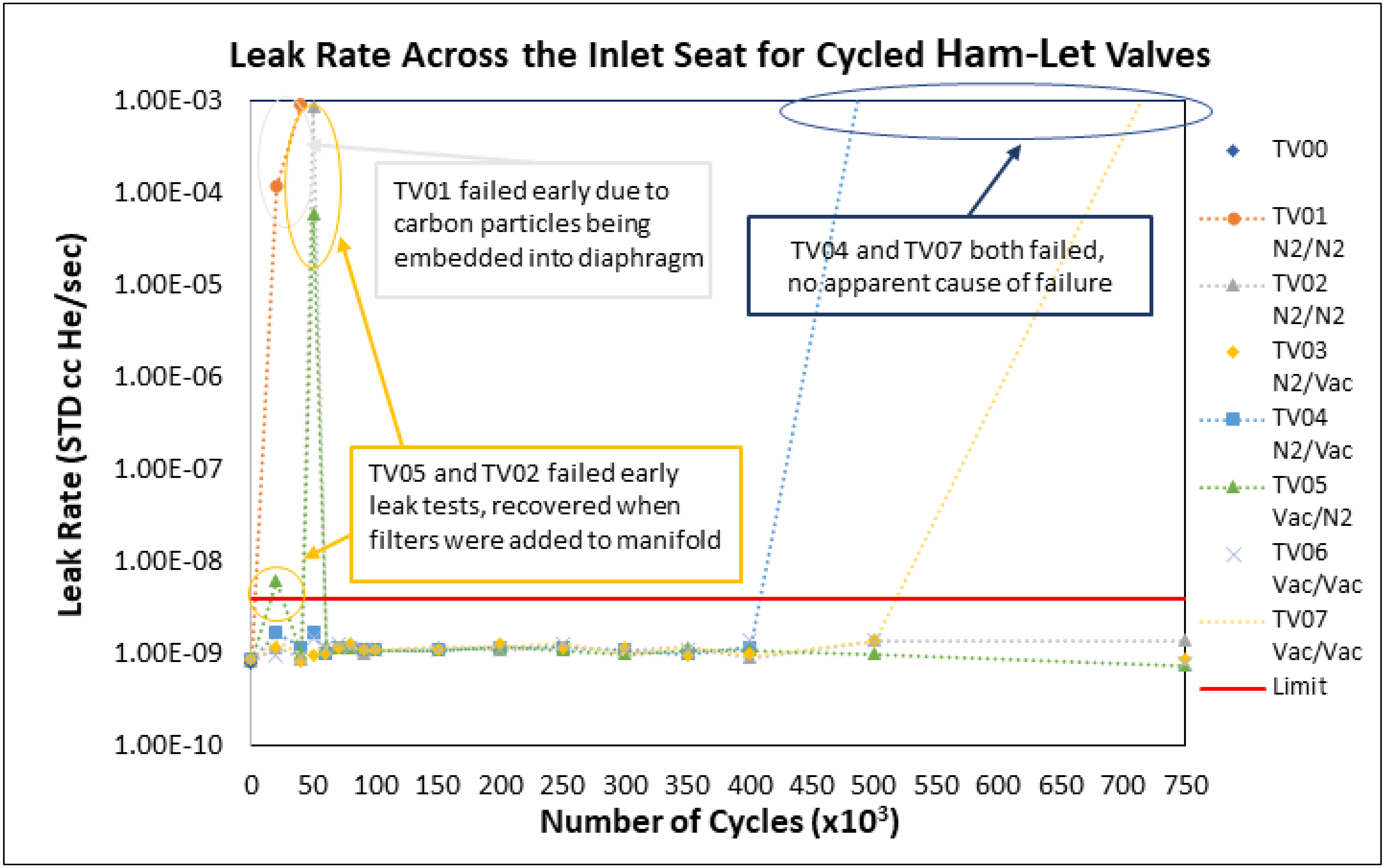


Figure 2-3. Inlet Seat Leak Rates for Nitrogen-Cycled Ham-Let Valves

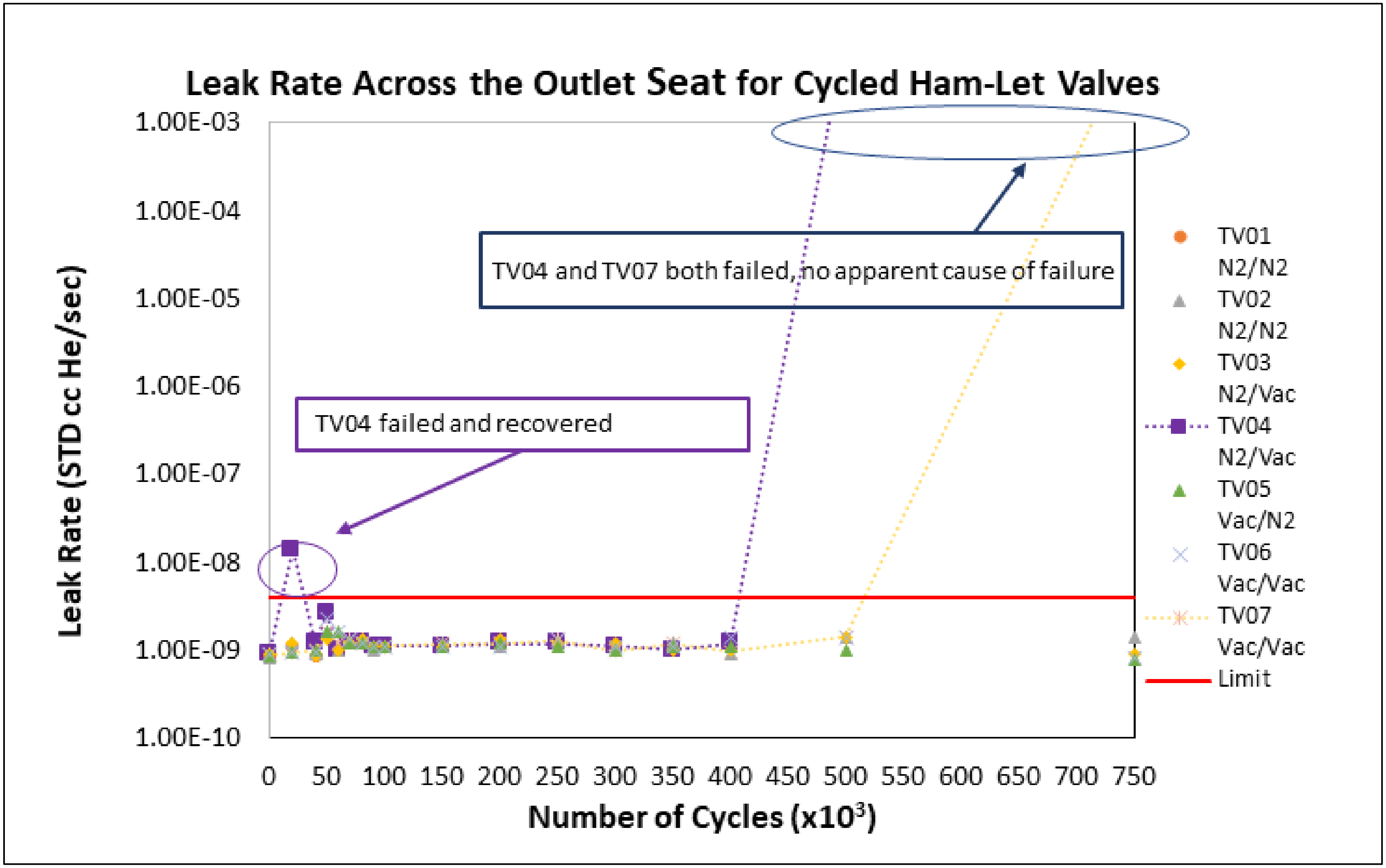


Figure 2-4. Outlet Seat Leak Rates for Nitrogen-Cycled Ham-Let Valves

2.1.3 Failure Analysis of Nitrogen-Cycled Valves

A total of three diaphragm valves failed during nitrogen cycling tests, though only one failed within the manufacturer's stated 100,000 expected cycle life as described in the 2017 report [9]. The other two diaphragm valves failed at 500,000 and 750,000 cycles – which greatly exceeds their estimated cycle life. The failure mechanism for each of each valve was examined. Leak testing identified failures and characterization of the failed diaphragms was performed to determine causes. Body leak testing, where the inside of a test item is pressurized with helium while the outside is under vacuum and monitored for helium, identifies valve leakage, but does not identify the leak location.

Table 2-2 shows valve TV01 leak test failure at 20,000 cycles was not due to a valve body leak, but due to a leak across the valve seat. Valves failures at greater cycle numbers (TV04 and TV07) failed inlet and outlet valve leak tests as well as body leak test with the body leaks rates exceeding the range of the leak detector.

Table 2-2. Body Leak Rates Comparison of Nitrogen Cycled Valves

Valve ID	# Cycles at Failure	Body Leak Rate Initial	Body Leak Rate at Failure
TV01	20,000	$<1.1\text{x}10^{-09}$	$<8.4\text{x}10^{-10}$
TV04	500,000	$<8.8\text{x}10^{-10}$	$>1.4\text{x}10^{-04}$
TV07	750,000	$<9.0\text{x}10^{-10}$	$>1.4\text{x}10^{-04}$

Valves TV04 and TV07 were disassembled and analyzed to understand the failure mechanism of the valves. Figure 2-5 and Figure 2-6 are photographs of post-test valve TV07 diaphragms with valve diaphragm locations illustrated in Figure 2-7. Visual inspection of the diaphragms did not show obvious signs of damage indicating valve failure. The diaphragms do have some markings showing the interaction with the actuator button seat; valve TV04 diaphragms showed similar markings but are not included here.

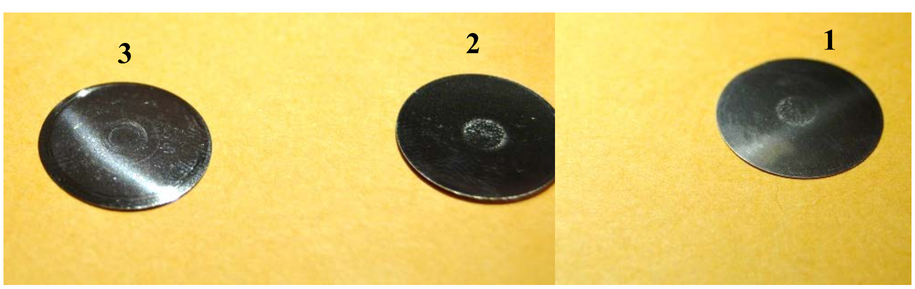


Figure 2-5. Diaphragms of TV07 Facing the Fluid: Top (3), Middle (2), and Bottom (1)

Figure 2-6. Diaphragms of TV07 Facing the Actuator: Top (3), Middle (2) and Bottom (1)

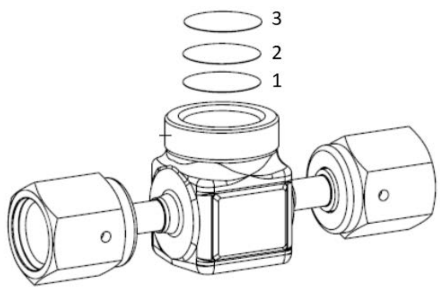


Figure 2-7. Ham-Let Diaphragm Valve Diagram

Figure 2-8 shows signs of spotting on the top and bottom of the diaphragms for TV01 [9]. TV01 diaphragms were examined using a scanning electron microscope (SEM) after they were cycled 100,000 times because the spots were not present in valves that were not cycled. By utilizing the SEM equipped with an energy-dispersive X-ray spectroscopy detector (EDS), the surface was imaged to identify the source of the contamination.

Figure 2-8. Diaphragms from TV01 Showing Spotting After Failure

From SEM images comparing an uncycled valve to TV01, as shown in Figure 2-9, there were large defects in the surface of TV01 that were not there present prior to cycling. After defects were discovered on the surface while imaging, EDS spectra were taken of the suspect locations. The insets in Figure 2-10 reveals the chemical composition of the bulk surface, cobalt, since the main element in the diaphragm alloy is cobalt, while the foreign material that appears embedded are comprised of carbon. From the EDS spectra, Figure 2-11, also shows the bulk of the material is cobalt with small quantities of carbon present. The source of carbon is unknown, though it is possible that particulates (Teflon) from an isolation valve could have been embedded into the diaphragms prior to the installation of the filters. The particulate contamination theory could be extended to the early failure of TV02 and TV05 which then recovered once filters were added to the valve testing manifold. Isolation valve IV15, which is cycled each time the test valves are cycled, was replaced on the manifold after 40,0000 cycles after it started to make noises while cycling. IV15 was never examined for mode of failure.

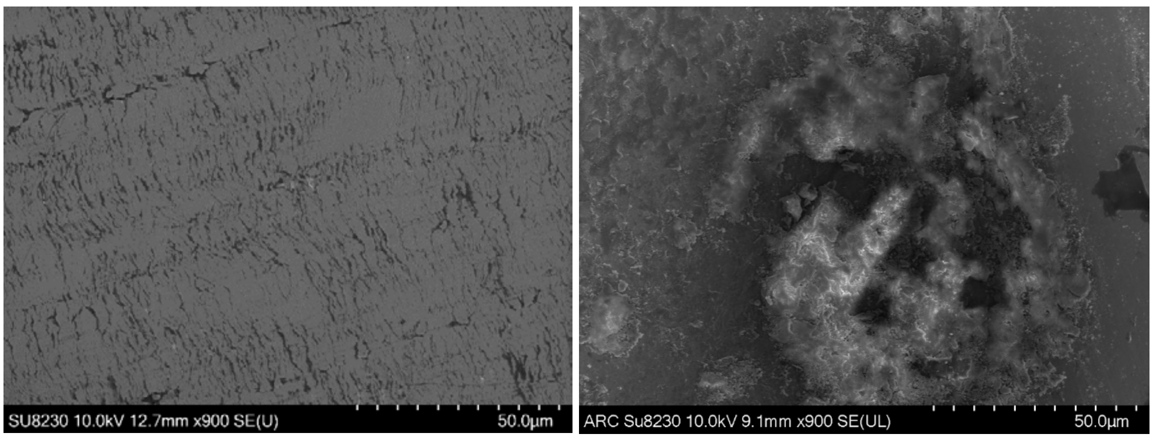


Figure 2-9. SEM Images of Non-Cycled Diaphragm (Left) and Cycled Diaphragm (TV01) (Right)

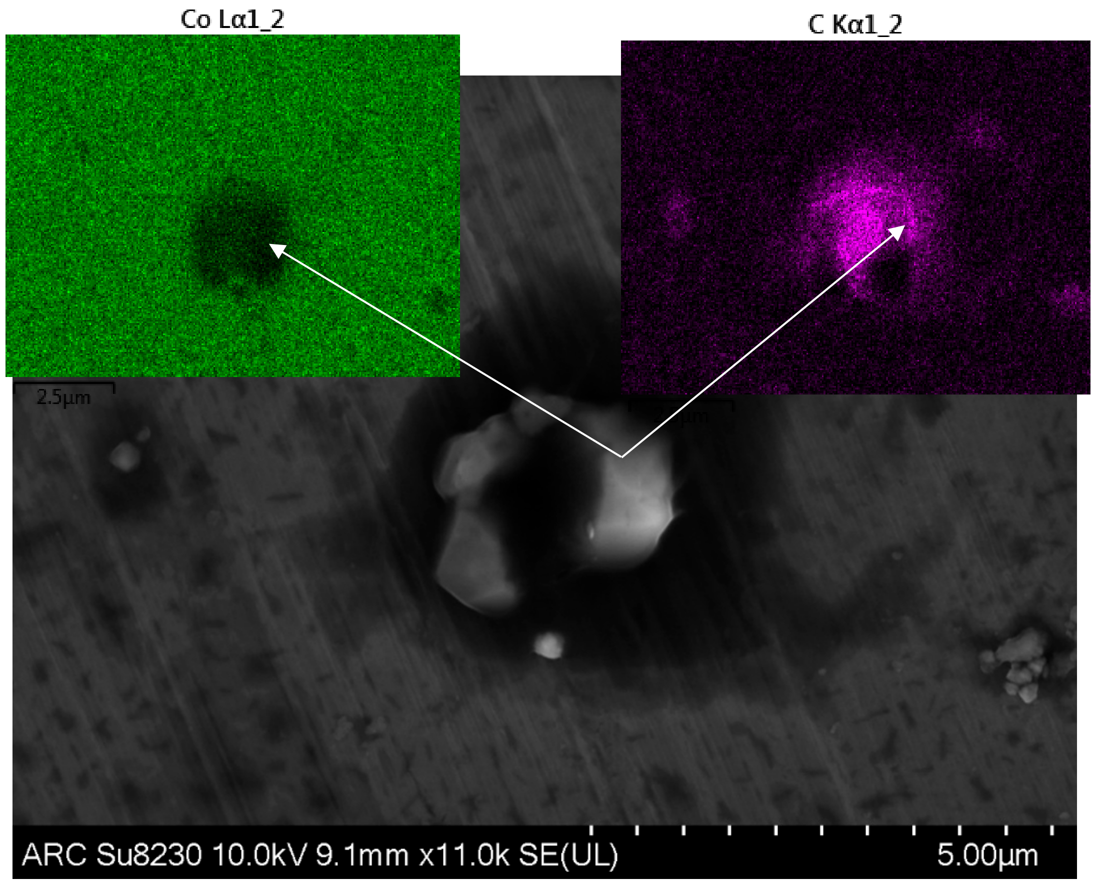


Figure 2-10. SEM image of TV01 with EDS spectrographic image insets showing locations of cobalt (Co) and carbon (C) in the sample, with large carbon particle highlighted with arrows

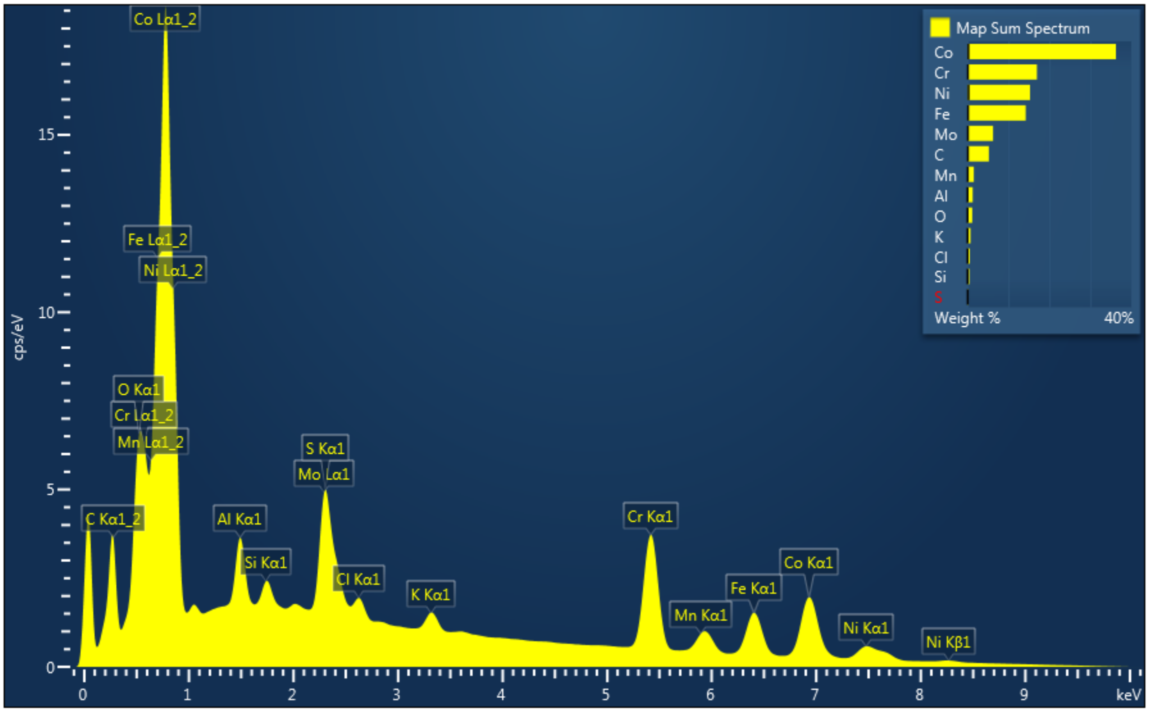


Figure 2-11. EDS Spectra of TV01 of Region from Figure 2-10

2.2 Diaphragm Valves Cycled in Hydrogen

Hydrogen embrittlement is a concern that could lead to failure for certain components, particularly for those components that see primarily hydrogen gases in a process system. Understanding the behavior of the diaphragm materials in a hydrogen environment is a key indicator that must be understood prior to tritium exposure.

Before cycling, the valves were exposed to 22 psig of protium (99.95% hydrogen) at 105°C for 1 month to simulate the hydrogen profile in the diaphragm material after 10 years of exposure at ambient temperature. To further accelerate the effects of hydrogen on the metal diaphragm, the valve bodies were heated to 105°C during cycle testing and a protium pressure of 50 psig was used for the tests. The valve cycling rate for these tests was also reduced to about 2 cycles a minute, allowing completion of 100,000 cycles in a nearly one month. The manifold would pressurize the valves then the gas would be exposed to the diaphragm for 24 seconds before starting the next valve cycle.

2.2.1 Experimental Set-Up for Hydrogen Cycling

The valve cycling manifold configuration for hydrogen gases is nearly identical to the nitrogen gas cycling manifold. Figure 2-12 is the diagram of the hydrogen valve testing manifold. For hydrogen cycling, five valves were tested and cycled for 125,000 cycles. The orientation of the valves matches the nitrogen valve apparatus, with two valves having hydrogen on the inlet and outlet, two valves having hydrogen on the inlet and vacuum on the outlet, and one valve having vacuum on the inlet and hydrogen on the outlet.

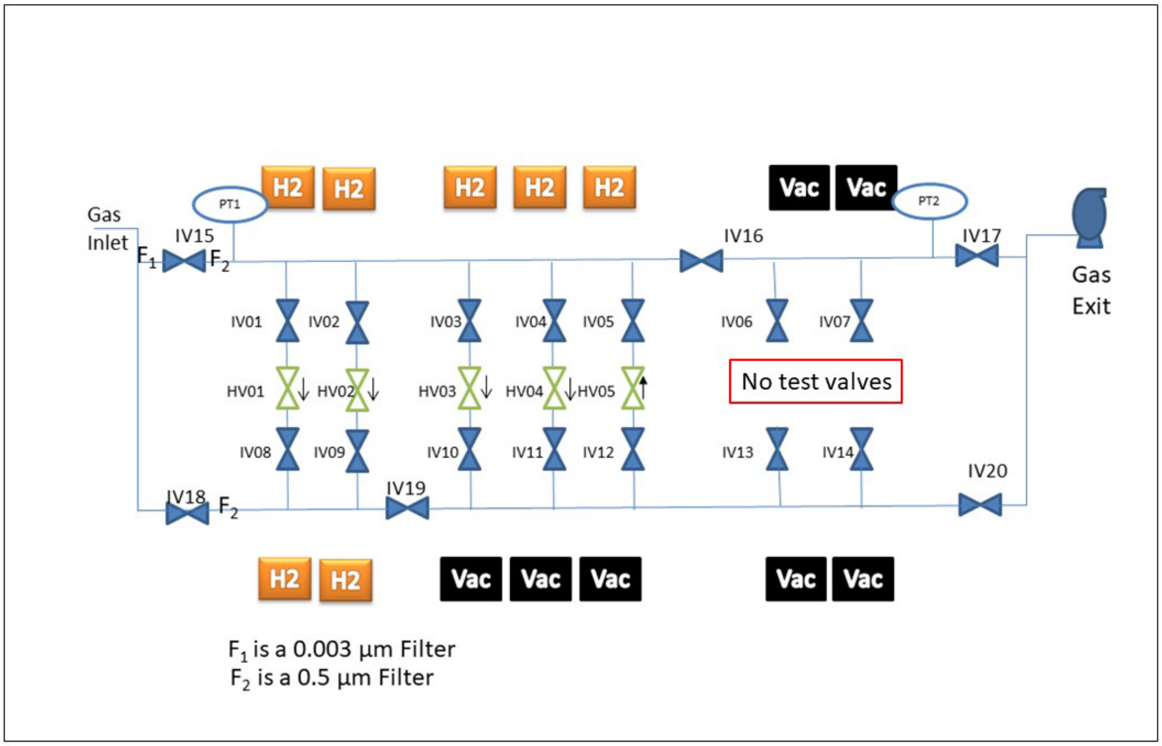


Figure 2-12. Hydrogen Valve Testing Manifold Diagram

For valve heating, heat tape was applied directly to the valve bodies, while minimizing heat to other parts of the valve. The heat tape was surrounded by an insulated wrap to retain heat and protect the plastic pneumatic tubing from elevated temperatures. A temperature controller with thermocouples secured to the body of one of the valves provided temperature control for all the valves. An interlock was added and attached to a different valve to ensure the valves would not exceed 150 ºC. Finally, another independent thermocouple was secured to a third valve body to measure and record the temperature during unsupervised cycling.

2.2.2 Hydrogen Experimental Cycling Results

A summary of valve leak test results is provided in Table 2-3. The valves underwent 125,000 cycles with valve leak checks performed nominally every 25,000 cycles. Two out of the five valves failed at ≥ 100,000 cycles. Valve HV01, cycled with hydrogen on the inlet and the outlet, failed at the 100,000 cycles leak test. Valve HV05, with vacuum on the inlet and hydrogen on the outlet, failed at the 125,000 cycles leak test. These two valves failed both the inlet seat leak test, shown in Figure 2-13, and the outlet leak test, as shown in Figure 2-14. Two valves, HV03 and HV05, failed the leak test criteria for the outlet seat at 80,000 cycles but recovered for the subsequent leak test after additional cycling. The unknown anomaly that caused this slight failure corrected itself during cycling.

Table 2-3. Leak Rates of Inlet and Outlet Seat for Hydrogen-Cycled Valves

Test Valve	HV01 H_2/H_2		HV02 H_2/H_2		HV03 H_2/Vac		HV04 H_2/Vac		HV05 Vac/H_2	
# of Cycles	Seat Inlet Leak[1]	Seat Outlet Leak [1]	Seat Inlet Leak[1]	Seat Outlet Leak [1]	Seat Inlet Leak[1]	Seat Outlet Leak [1]	Seat Leak Inlet[1]	Seat Outlet Leak [1]	Seat Inlet Leak[1]	Seat Outlet Leak [1]
0	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$
25.000	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$
50,000	$< 1.3 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$
80,000	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 8.8 \times 10^{-10}$	$< 8.8 \times 10^{-10}$	$< 1.4 \times 10^{-9}$	5.0×10^{-9}	$< 1.4 \times 10^{-9}$	$< 1.4 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	6.6×10^{-9}
100,000	$\sim 1.0 \times 10^{-4}$	$\sim 1.0 \times 10^{-4}$	$< 5.6 \times 10^{-10}$	$< 5.6 \times 10^{-10}$	$< 5.7 \times 10^{-10}$	$< 5.7 \times 10^{-10}$	$< 9.6 \times 10^{-10}$	$< 9.6 \times 10^{-10}$	$< 1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$
125,000	X	X	$< 1.3 \times 10^{-9}$	$< 1.3 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$< 1.2 \times 10^{-9}$	$<1.1 \times 10^{-9}$	$< 1.1 \times 10^{-9}$	X	X

Notes:
A passing leak rate is defined as 4.00 x 10^{-9} STD cc He/sec or less.
[1] Leak Rates in STD cc He/sec
X Denotes the Leak Rate is a Higher than Detectable by the Helium Mass Spectrometer Detection

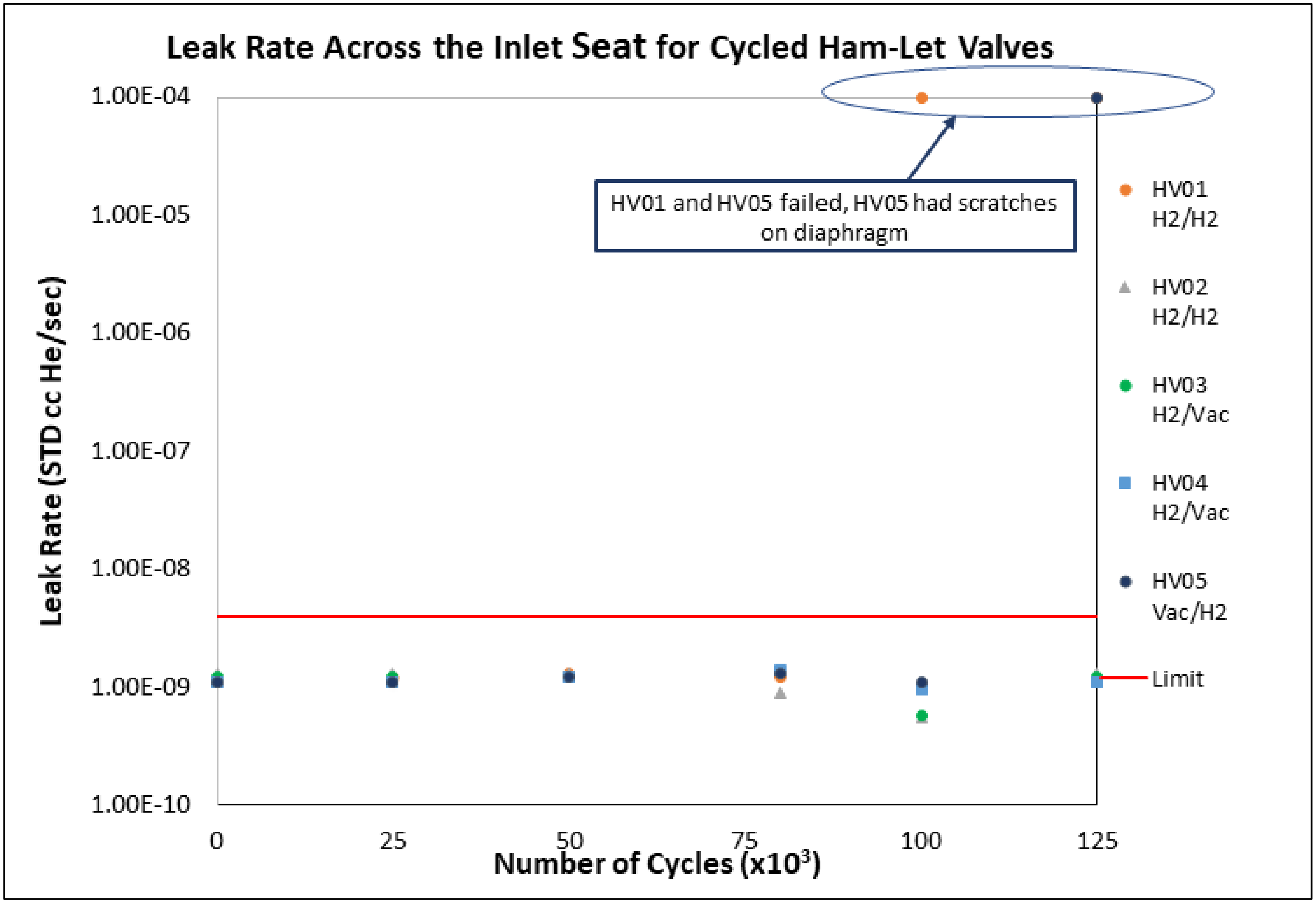


Figure 2-13. Leak Rates Across the Inlet Seat for Hydrogen-Cycled Valves

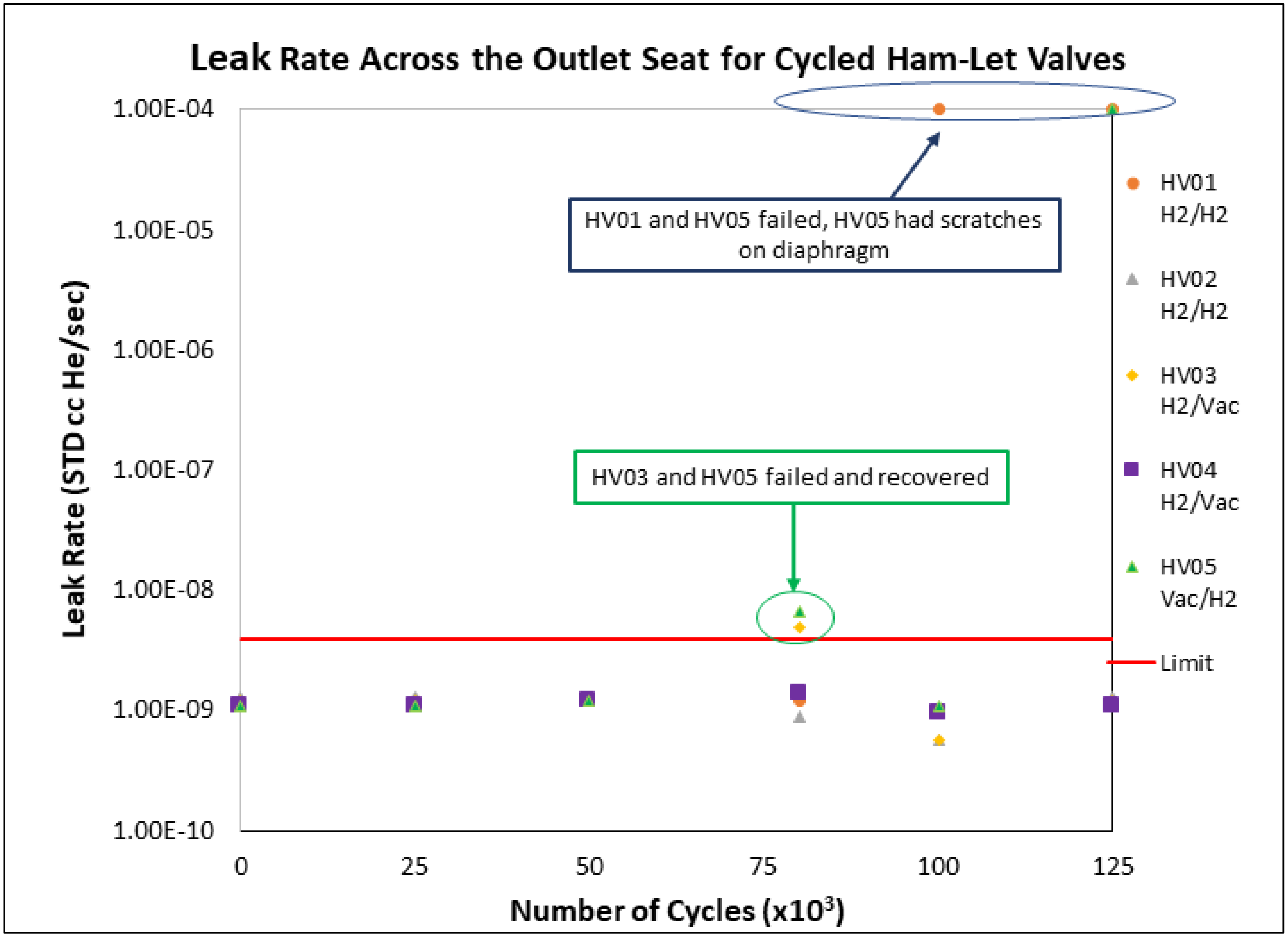


Figure 2-14. Leak Rates Across the Outlet Seat for Hydrogen-Cycled Valves

2.2.3 Failure Analysis of Hydrogen-Cycled Valves

All five valves attained the manufacturer's stated life expectancy of 100,000 cycles - even cycling in 50 psig hydrogen at 105ºC. Comparing the body leak rates of the two failed valves at failure to initial body leak rates, shown in Table 2-4, reveals that the leak rates of the valve body remains unchanged. The valves were disassembled, and the diaphragms visually examined for evidence of valve failure. Neither sides of the HV01 diaphragms showed obvious signs of wear from cycling, as shown in Figure 2-15 and Figure 2-16.

Table 2-4. Body Leak Rate Comparison of Hydrogen Cycled Valves

Valve ID	# of Cycles at Failure	Body Leak Rate Initial	Body Leak Rate at Failure
HV01	100,000	$<1.2\times10^{-09}$	$<1.3\times10^{-09}$
HV05	125,000	$<1.1\times10^{-09}$	$<1.2\times10^{-09}$

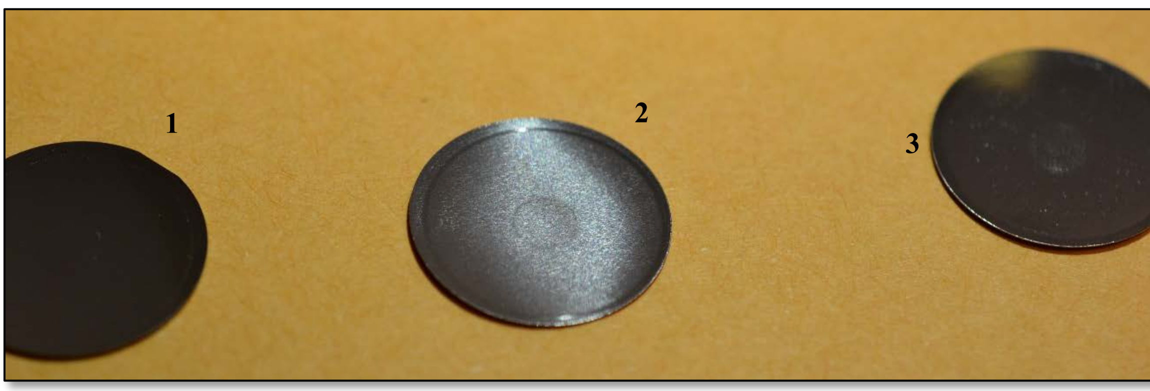


Figure 2-15. Diaphragms of HV01 Facing the Fluid: Bottom (1), Middle (2), and Top (3)

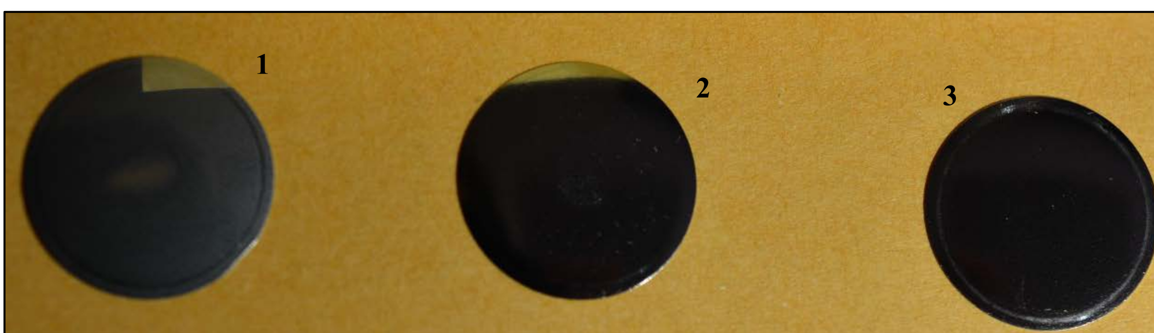


Figure 2-16. Diaphragms of HV01 Facing the Actuator: Bottom (1), Middle (2), and Top (3)

However, the diaphragm of Valve HV05 showed a surface modification compared to that of both the uncycled valves and HV01 after failure on the surface facing and closest to the vacuum, as shown in Figure 2-17. There is evidence of extensive surface anomaly towards the center of the diaphragm as well with some unknown defects towards the edge, shown in the enlarged view of Figure 2-18. The middle diaphragm also had some surface modifications on the outer edge as well. The dulling/lack of luster on the fluid facing side of the valve is an artifact of the photography and the angle of photograph to show the defects, the valves appear similar on both sides. The backside of HV05, facing the actuator, appears unchanged after with minimal damage from cycling, which is viewed in Figure 2-19. No additional characterization of HV05 has been performed to identify the potential root cause of the valve leak rate failure.

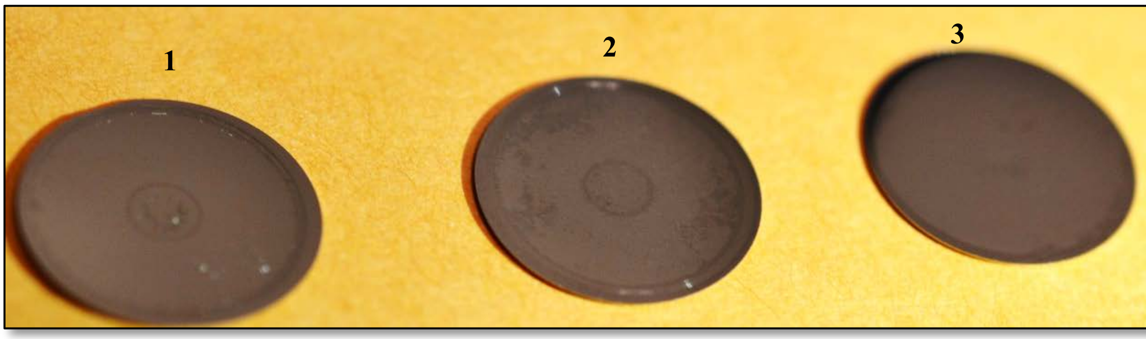


Figure 2-17. Diaphragms of HV05 Facing the Fluid: Bottom (1), Middle (2), and Top (3)

Figure 2-18. Fluid Facing-Bottom Diaphragm from HV05, Visible Surface Modifications to the Middle of the Diaphragm and Outer Edge

Figure 2-19. Diaphragms of HV05 Facing the Actuator: Bottom (1), Middle (2), and Top (3)

3.0 Discussion

Of the seven valves cycled in nitrogen, TV01 failed the $4.0x10^{-9}$ STD cc He/sec leak rate criteria when tested after 20,000 cycles – well less than the anticipate cycle life of 100,000 cycles. The valve failure was attributed to polymeric debris embedded in the diaphragm. This conclusion is further supported by the valve body leak rate of TV01 meeting the leak rate criteria while other valve failures had body leak rates exceeding the leak rate criteria.

The manifold placement of TV01 closest to the test gas supply supports supposition manifold debris, up to the gas supply, may have primarily entered this valve causing early failure. The failure and subsequent recovery of valve performance by valves TV04 and TV05 after installation of filters in the test manifold demonstrates that control of particulates in the process lines is important for reliable valve operation.

Nitrogen cycled failed valves TV04 and TV07 both failed the body leak rate criteria after 500,000 cycles or more, but no direct causality could be assigned to the failure mechanism. The only commonality between TV04 and TV07 was each valve had vacuum on the outlet of the valve during cycling. However, each valve having a “twin” valve (same test conditions and valve orientation) with each having a greater cycle life (at least 750,000 cycles) than the failed valve demonstrates no common failure mechanism for these valves.

Of the five valves cycled in hydrogen, valves HV03 and HV05 had failed and subsequently had recovered valve performance. Failure leak rates of $5.0x10^{-9}$ STD cc He/sec and $6.6.0x10^{-9}$ STD cc He/sec for HV03 and HV05, respectively, would not likely be noticed during process valve usage but were reported as failures since the measured leak rates did exceed the $4.0x10^{-9}$ STD cc He/sec criteria.

Heated, hydrogen-cycled failed valves HV01 and HV05 both passed the body leak rate criteria after 100,000 cycles or more indicating the failure mechanism to be the sealing of the diaphragm to the valve body. A commonality between HV01 and HV05 was hydrogen on the outlet of the valve during cycling. However, HV01 having a twin valve (HV02) with a greater cycle life (at least 125,000 cycles) demonstrates no direct common failure mechanism for the valves.

It is not clear if cycling the valves in hydrogen, at elevated temperature, or some other factor contributed to the hydrogen cycled valves having an apparent lower cycle life than nitrogen cycled valves. Surface irregularities where present on a diaphragm of a failed valve, but no cause was determined. The use of 99.95% hydrogen (500 ppm impurities) may have created reaction products on the diaphragm of the valves which inhibited sealing of the diaphragm with the valve body, but further examination of the diaphragms would be needed to support this conjecture.

An important consideration for use of these valves in tritium systems is the confinement of tritium for a failed valve. Valve "seat" failures - inadequate sealing of the diaphragm onto the valve from particulate contamination, would not create tritium leaks out of the valve, but diaphragm failures creating a body leak rate failure would. The lack of secondary confinement for these valves (e.g. a confinement bellows) may limit or eliminate their use in air hoods but use of these valve may be acceptable when secondary confinement is utilized (i.e. a glovebox). Valves used within the stated lifetime of 100,000 cycles were found to pass the body leak rate criteria indicating they would likely confine the tritium process gas if valve service life was limited. Design parameters, such as the total number of valve cycles and the need for secondary confinement upon valve failure, would need to be considered for deployment of these valves in tritium systems.

Tritium testing would further validate the suitability of these valves for tritium service. The tritium permeation flux from the valve through the diaphragms would need to be evaluated. The effects of helium-3 (produced by the decay of tritium) on the cycle life of the valve/diaphragm(s) would also need evaluation.

4.0 Conclusions

All-metal diaphragm valves offer an alternative to the use of polymer-tipped bellow sealed valves for tritium gas processing systems. The Ham-Let Group 3LE Series valve is an all-metal diaphragm valve selected for evaluation. Valve cycle tests using nitrogen at ambient temperature showed the Ham-Let valves can greatly exceed the vendor's stated valve cycle limit of 100,000 cycles if particulates are controlled in the system: up to 500,000 cycles or more, for the valves tested.

Valves cycle tested at 105°C using 99.95% hydrogen at 50 psig can meet or exceed the vendor's stated valve cycle life, but the cause of valve (diaphragm sealing) failure needs further investigation to determine if hydrogen, heating, or some other factor lessened the valve cycle life relative to the nitrogen cycled valves.

The flux of tritium from the valve and the impact of He-3 on the mechanical properties of the valve diaphragm may ultimately determine the suitability of these types of valves in tritium processes. Tritium exposure of the diaphragm materials followed by destructive evaluation would give insight into the effects of He-3 on the diaphragms. Deployment of a test valve in a non-critical tritium process location would also aid the evaluation of these valves for further deployment in tritium systems.

5.0 Acknowledgements

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