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CAUSES AND MITIGATION OF FUEL VALVE PILOT SEAL EXTRUSION IN SPACE SHUTTLE ORBITER PRIMARY RCS THRUSTERS

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ABSTRACT

Extrusion of a polytetrafluoroethylene (PTFE) pilot seal located in the Space Shuttle Orbiter Primary Reaction Control Subsystem (PRCS) thruster fuel valve has been implicated in 68 ground and on-orbit fuel valve failures. A rash of six extrusion-related in-flight anomalies over a six-mission span from December 2001 to October 2002 led to heightened activity at various NASA centers, and the formation of a multidisciplinary team to solve the problem. Empirical and theoretical approaches were used. For example, thermomechanical analysis (TMA) and exposure tests showed that some extrusion is produced by thermal cycling; however, a review of thruster service histories did not reveal a strong link between thermal cycling and extrusion. Calculations showed that the amount of observed extrusion often exceeded the amount allowed by thermally-induced stress relief. Failure analysis of failed hardware also revealed the presence of fuel-oxidizer reaction product (FORP) inside the fuel valve pilot seal cavity, and differential scanning calorimetry (DSC) showed that the FORP was intimately associated with the pilot seal material. Component-level exposure tests showed that FORP of similar composition could be produced by adjacent oxidizer valve leakage in the absence of thruster firing. Specific gravity data showed that extruded fuel valve pilot seals were less dense than new pilot seals or oxidizer valve pilot seals, indicating permanent modification of the PTFE occurred during service. It is concluded that some thermally-induced extrusion is unavoidable; however, oxidizer leakage-induced extrusion is mostly avoidable and can be mitigated. Several engineering level mitigation strategies are discussed.

INTRODUCTION

Pilot operated valves (POVs) are used to control the flow of hypergolic liquid propellants monomethylhydrazine (fuel) and nitrogen tetroxide (oxidizer) to the Shuttle orbiter Primary Reaction Control Subsystem (PRCS) thrusters. The POV incorporates a two-stage design: a solenoid-actuated pilot stage, which in turn controls a pressure-actuated main stage. Isolation of propellant supply from the thruster chamber is accomplished in part by a captive

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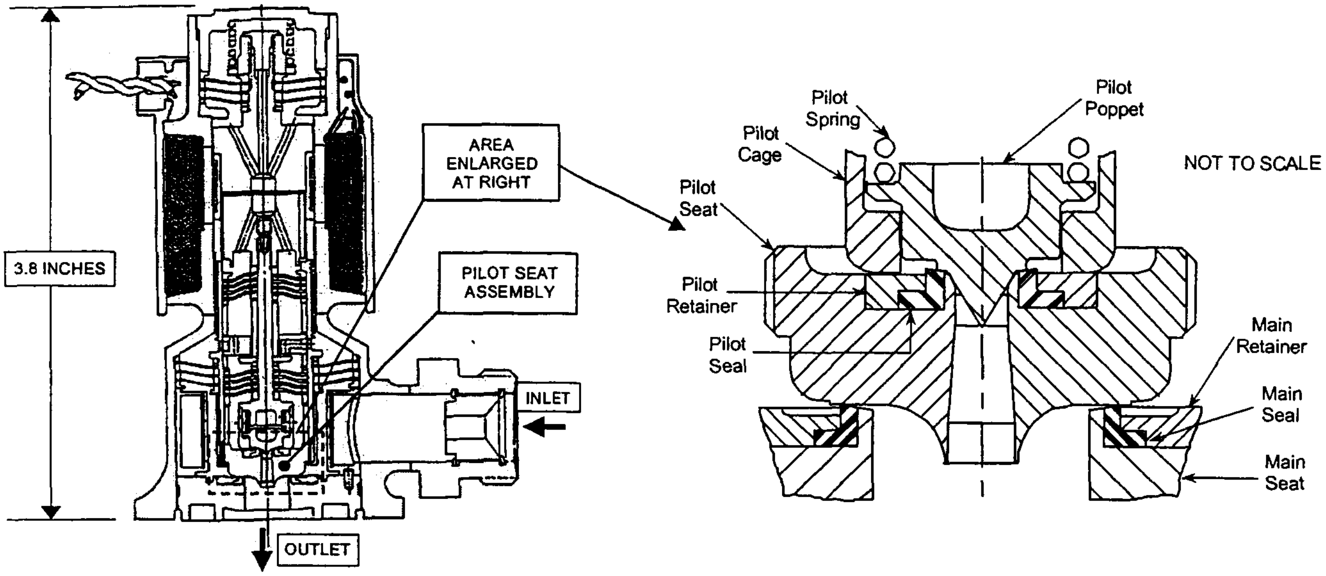

Figure 1 Pilot operated valve cross section showing the location of the polytetrafluoroethylene pilot seal.

polytetrafluoroethylene (PTFE) Teflon 7A®[*] pilot seal retained inside a Custom 455®[†] (C455) stainless steel cavity (Figure 1).[‡]

Extrusion of the pilot seal restricts the flow of propellant around the pilot poppet, thus impeding or preventing the main valve stage from opening. It can also prevent the main stage from staying open with adequate force margin, particularly if there is gas in the main stage actuation cavity. During thruster operation on-orbit, pilot seal extrusion may be indicated by low or erratic chamber pressure (low Pc) or failure of the thruster to fire upon command (Fail-Off). During ground servicing, pilot seal extrusion may be indicated by slow gaseous nitrogen (GN$_2$) main valve opening times (≥ 38 ms), slow water main valve opening response times (> 33 ms), shallow pressure drop or liquid flow perturbation across the main stage, or an abnormally shaped (off-nominal) valve opening response current trace. Poppet lift tests and x-ray radiography have also been used to determine the presence of pilot seal extrusion during ground servicing. While the above tests are nondestructive; the most reliable means to characterize and quantify extrusion is post-mortem metrology performed on removed pilot seat assemblies (Marquardt P/N 235681).

Other known discriminators for fuel valve pilot seal extrusion are:

- The vast majority of extrusion cases have involved fuel valve pilot seals. Oxidizer valve pilot seals, by contrast, usually fail due to spontaneous oxidizer absorption, seal softening and deformation, and ultimately leakage.
- A review of selected original equipment manufacturer (OEM) Failure Malfunction Reports (FMRs) issued during *ca.* 1987-88 during the thermal insulation protective system modification (TIPS MOD), which involved ground acceptance testing if all fleet thrusters, yielded little evidence of slow GN$_2$ response (GN$_2$ data not always available).[§]
- All failures occurred after mission and ground turnaround exposure.
- There are no known failures of newly rebuilt hardware that saw routine processing.

The reason oxidizer valve pilot seals (average proud height[¶] = 41 ± 23 µm (1.6 ± 0.9 mil), n= 21) do not extrude as much as fuel valve pilot seals (average proud height = 144 ± 79 µm (5.7 ± 3.1 mil), n= 36) is threefold. First, oxidizer valves are newer than fuel valves on average due to a higher failure rate (220 oxidizer valves with documented mission firing

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[*] Teflon® is a registered trademark of E. I. DuPont and Nemours and Company, Wilmington, DE.

[†] Custom 455® is a registered trademark of Carpenter Technology Corporation, Reading, Pennsylvania.

[‡] Propellant isolation is also accomplished by the main poppet/seat.

[§] Ross, B., Private communication. Boeing Human Space Flight and Exploration, White Sands Test Facility, Las Cruces, New Mexico. May 2002.

[¶] The proud height is the height of the inner diameter edge of PTFE pilot seal above the downstream metal seat.

history replaced since 1981, versus 110 fuel valves). Second, evaporative cooling of oxidizer (boiling point = 21 °C (70 °F)) compared to the fuel (boiling point = 88 °C (190 °F)) reduces the amount of heat soakback after thruster firing that reaches the oxidizer valve pilot seal. Third, the pilot seal material of construction, Teflon 7A PTFE, spontaneously absorbs oxidizer (up to 3.8 percent (w/w) oxidizer after 7 weeks[1]), leading to reversible property changes such as softening[2] and reduction of crystallinity.[3] This results in increased deformation of the pilot seal under poppet loading, and in the worst case scenario, metal-to-metal contact and oxidizer leakage.

Minimizing PRCS fuel valve pilot seal extrusion has become an important issue in the effort to improve PRCS reliability and reduce associated life cycle costs. Also, given the unacceptable consequences of multiple thruster failures occurring on the same attitude control axis (mission termination or loss of vehicle control), it became imperative to determine the cause(s) of extrusion. Only then could appropriate engineering controls be formulated and implemented to mitigate further occurrence.

Extrusion Mechanisms

Soon after the first documented extrusion-related failure in 1994, two mechanisms were proposed to explain fuel valve pilot seal extrusion.[4] The first mechanism involves thermal expansion mismatch of adjacent plastic (PTFE) and metal (C455) materials of construction, leading to gradual extrusion of the pilot seal. For example, the coefficient of thermal expansion of PTFE (1.24×10^{-4} °C^{-1} for T = 25 to 100 °C (77 to 212 °F)[5] is more than one order of magnitude greater than that of C455 (1.06×10^{-5} °C^{-1} for T = 21 to 93 °C (72 to 200 °F).[6] This type of extrusion is referred to as *thermal extrusion*, and was thought to be caused by excessive or prolonged thermal cycles on-orbit (during thruster firing or solar heating), during ground processing (during vacuum bake-outs to remove water or epoxy coating curing repairs), or during part fabrication (during part welding operations).

The second mechanism involves oxidizer leakage from the adjacent oxidizer valve on the same thruster during ground turnaround operations at Kennedy Space Center (KSC), leading to reaction with MMH, and culminating in the production of fuel-oxidizer reaction product (FORP) and liberation of large quantities of heat and gas in or near the fuel valve pilot seal or pilot seal cavity, leading in turn to more rapid extrusion of the pilot seal. This type of extrusion is referred to as *oxidizer-induced extrusion*, and has been traced to the installation of a universal throat plug accessory (UTPA) in 1991. The purpose of the UPTA was twofold: 1) to prevent moisture intrusion and alleviate associated nitric acid-corrosion problems, and 2) to prevent exposure of ground personnel to propellants. However, as an unintended consequence, the UTPA was later found to increase oxidizer vapor concentrations near the fuel valve.

A rash of oxidizer valve leakage during the early 1990s, coupled with clogging of the UTPA orifice during 1995-96 (exacerbating oxidizer build-up), and subsequent implementation of a necessarily discontinuous gaseous nitrogen (GN_2) trickle purge beginning in 1998, did not eliminate high oxidizer vapor concentrations.[#] The potentially adverse consequences of having high oxidizer vapor concentrations and 1.82 MPa (264 psia) pressurized fuel on opposite sides of a 330-μm (13 mil) wide pilot seal-poppet sealing interface are fairly apparent. However, finding conclusive documentation, or firm theoretical or empirical grounds to link extrusion with oxidizer valve leakage turned out to be nontrivial.

Failure History and Distribution

Extrusion was first documented after thruster Serial Number (S/N) 325 Failed-Off during Space Transportation System Flight (STS)-68 in December 1994.[4,7] Through 2002 and including the STS-68 S/N 325 failure, there have been a total of ten In-Flight Anomalies (IFAs) attributed directly to extrusion of the pilot seal (Table 1, top):

- 8 Fail-Off IFAs: S/Ns 325 (STS-68), 101 (STS-81), 451 (STS-83), 628 (STS-91), 101 and 330 (STS-108), 215 (STS-110), and 229 (STS-112)
- 2 low Pc IFAs: S/Ns 411 and 484 (both during STS-110)

A rash of six extrusion-related IFAs over a six-mission span from Dec. 2001 to Oct. 2002 (on STSs-108, -110, and -112) led to heightened activity at various NASA centers, and the formation of a multidisciplinary team to solve this problem. IFAs (6) for which extrusion was not implicated,[**] but was detected during follow-up ground testing are as follows (Table 1, top):

- 1 Heater Fail-Off IFA: S/N 616 (STS-77)

[#] Fuel valve S/N 764 (thruster S/N 411), for example, which failed after only 5 missions, had a history of adjacent oxidizer valve leakage, and was plagued by problems with an effectively administered GN_2 trickle purge.

[**] Fitzgerald, E. , Private communication, OMS-RCS NASA Johnson Space Center, Houston, TX. October 2003.

- 2 Fail-Leak IFAs: S/Ns 476 (STS-67) and 219 (STS-88)
- 3 Fail-Off IFAs: S/Ns 574 (STS-72), 234 (STS-76), and 498 (STS-95)

In addition to the above 16 IFAs, another 52 fuel valves (Table 1, bottom; Table 2) with extruded pilot seals were detected between 1994 and 2003 during routine and nonroutine thruster repair and replacement (R&R) at the NASA Johnson Space Center (JSC) White Sands Test Facility (WSTF) Depot, giving a total of 68 extrusion cases. The overall flight plus ground extrusion failure rate has remained fairly constant since 1994,[††] with the number of failures typically peaking in years when entire ship sets are returned for water flushing to remove metal nitrate salts (Figure 2).

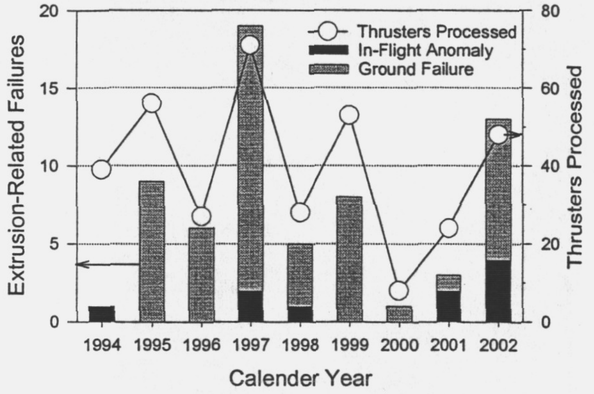

Figure 2 Distribution of PRCS fuel valve pilot seal extrusion cases from 1994 to 2003.

Before STS-68, another 39 fuel valves with mission history were replaced by the OEM (Marquardt, Van Nuys, California; now Aerojet, Redmond, Washington). Gypsum intrusion after the 1982 STS-3 landing, the Shuttle Orbiter Forward Reaction Control Pod Number 2 (FRC2) Power-On anomaly during the 1986 STS-61C flow, and ground screening tests during the 1986-1988 TIPS-MOD overhaul lead to most of the pre-STS-68 fuel valve repairs. Although extrusion is suspected or has been verified in 96-percent (68 of 71) of the fuel valve failures since STS-68, visual examination of selected pilot seals taken from valves that failed before STS-68 did not show severe extrusion.[‡‡] A review of Marquardt FMRs issued during the 1986-88 TIPS MOD also gave no conclusive evidence of extrusion. Consequently, it may be inferred that extrusion is a more recent phenomenon.

Extrusion Types

Two types of fuel valve pilot seal extrusion have been observed: extrusion of the entire seal across the sealing (inner diameter, *id*) and nonsealing (outer diameter, *od*) surfaces of the pilot seal (*Type I extrusion*); and preferential extrusion of the non-sealing (*od*) surface of the pilot seal (*Type II extrusion*) (Figure 3).[§§]

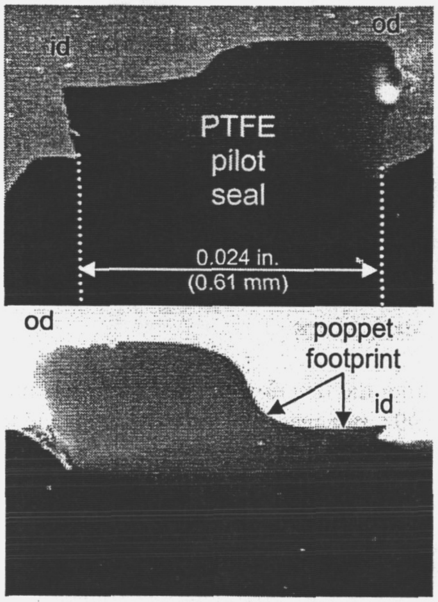

Figure 3 Impression replicas of fuel valve pilot seals showing Type I (top) and II (bottom) extrusion.

EXPERIMENTAL

Service History Correlations

Firing history data through STS-113 (flown November 2002) were obtained from JSC OMS/RCS Operations. Available firing history data were combined with fuel valve R&R histories obtained from WSTF Depot (*PRCS Major Configuration Table*)[¶¶] and KSC Reusable Space Systems. This

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[††] On average, about one extrusion case is observed for every three thrusters removed from the fleet and processed. A plot of thrusters processed versus number of thrusters failed due to extrusion gave a linear correlation coefficient, R^2, of 0.77.

[‡‡] Wichmann, H. Private communication. Consultant, L&M Technologies, White Sands Test Facility, Las Cruces, New Mexico. December 2001.

[§§] An arbitrary proud height of 64 μm (2.5 mil) was the established break point between Type I and Type II extrusion.

[¶¶] In-house document. *PRCS Major Configuration Table.* WSTF intranet at S4\:wstfgrp\prop\depot\p-config\ps-config.mdb, NASA Johnson Space Center White Sands Test Facility, Las Cruces, New Mexico, most recent update.

Table 1

Thrusters involved in IFAs (top) and detected during ground ATP through 2003 (bottom)

Case No.	Thruster S/N	Fuel Valve S/N	Fu Valve Retainer Weld Type	Ox Valve S/N	Ox Valve R&Red at same time as Fuel Valve	Last STS	Last Mission Date	Years in Service	Burns	Ontime (s)	Seal ID Height (in.)	Seal OD Height (in.)	Extrusion Type	Basis for Extrusion	Why Pulled?	IFA Caused by Fuel Valve Pilot Seal Extrusion
Extrusion Cases Detected After IFAs																
1	101	254	I	510	No[a]	81	Jan-97	9.4	36	13	0.0093	0.0183	Type I	GN2 & water Mo, Met	IFA-Fail Off	Yes
2	101	544	I	510	Yes	108	Dec-01	4.6	286	138	0.0100	0.0199	Type I	GN2 & water Mo, Met	IFA-Fail Off	Yes
3	215	708A	I	528	Yes	110	Mar-02	13.9	686	1028	0.0136	0.0199	Type I	GN2 Mo, Met	IFA-Fail Off	Yes
4	219	525	C	775	No[b]	88	Dec-98	17.3	1772	432	0.0035	0.0095	Type I	GN2 Mo & Mc, Met	IFA-Fail Leak	No
5	229	708	I	724	No[b]	112	Oct-02	4.2	3114	429	0.0106	0.0155	Type I	GN2, Met	IFA-Fail Off	Yes
6	234	528	C	729	Yes	76	Mar-96	14.3	1772	754	0.0060[c]	ND	Type I	water Mo, PLT	IFA-Fail Off	No
7	325	530	C	251	No	68	Sep-94	10.3	6471	1068	0.0100	ND	Type I	GN2 Mo, Met	IFA-Fail Off	Yes
8	330	605	I	727	No[a]	108	Dec-01	5.5	660	72	0.0101	0.0237	Type I	GN2 and water Mo, Met	IFA-Fail Off	Yes
9	411	764	I	634	Yes	110	Mar-02	2.8	532	142	0.0035	0.0169	Type I	GN2 Mo, Met	IFA-low Pc	Yes
10	451	672	C	512	Yes	83	Apr-97	11.3	70	54	0.0033	0.0095	Type I	GN2 Mo,Met	IFA-Fail Off	Yes
11	476	703	I	703	No[b]	67	Feb-95	7.7	1278	375	0.0075[c]	ND	Type I	GN2 Mo, PLT	IFA-Fail Leak	No
12	484	749	C	713	No[a]	110	Mar-02	11.7	463	136	0.0063	0.0196	Type I	GN2 & water Mo	IFA-low Pc	Yes
13	498	762	I	767	Yes	95	Oct-98	6.3	309	141	ND	ND	Unknown	GN2 Mo	IFA-Fail Off	No
14	574	895	I	789	Yes	72	Jan-96	3.7	26	69	0.0034	0.0115	Type I	GN2 Mo, Met	IFA-Fail Off	No
15	616	823	I	830	Yes	77	May-96	5.4	929	728	0.0015[c]	ND	Type II	PLT (poor discriminator)	IFA-Heater Fail Off	No
16	628	832	I	827	Yes	91	Jun-98	7.0	2780	387	0.0075	0.0142	Type I	Met	IFA-Fail Off	Yes
Ground Failures (Unknown Type)																
1	119	241	C	784	No	112	Oct-02	21.6	3500	604	ND	ND	Unknown	GN2 Mo	OV 104 OMDP	...
2	133	255	C	561	Yes	77	May-96	15.7	2044	730	ND	ND	Unknown	GN2 Mo	OV 105 OMDP	...
3	220	516	C	758	Yes	70	Jul-95	13.7	6720	1229	ND	ND	Unknown	GN2 Mo	OV 103 OMDP	...
4	330	714	I	727	No	70	Jul-95	7.2	3752	818	ND	ND	Unknown	GN2 Mo	OV 103 OMDP	...
5	332	714	I	584	Yes	92	Oct-00	2.4	105	58	ND	ND	Unknown	GN2 Mo, PLT	PM flush	...
6	408	614	C	621	Yes	110	Feb-02	16.4	4146	872	ND	ND	Unknown	water Mo	PM Flush	...
7	427	630	C	620	Yes	93	Jul-99	14.4	1839	610	ND	ND	Unknown	GN2 Mo	OV 102 OMDP	...
8	430	588	C	666	Yes	77	May-96	11.5	2979	443	ND	ND	Unknown	GN2 & water Mo	OV 105 OMDP	...
9	452	581	C	644	Yes	105	Aug-01	16.1	369	502	ND	ND	Unknown	water Mo	OV 103 OMDP	...
10	457	573	C	671	Yes	112	Oct-02	15.2	1216	389	ND	ND	Unknown	GN2 Mo	OV 104 OMDP	...
11	463	646	C	673	No	93	Jul-99	10.6	989	1089	ND	ND	Unknown	GN2 Mo	OV 102 OMDP	...
12	488	208	C	204	Yes	81	Jan-97	8.4	3557	617	ND	ND	Unknown	water Mo	PM flush	...
13	615	814	I	820	Yes	93	Jul-99	8.5	378	385	ND	ND	Unknown	GN2 & water Mo	OV 102 OMDP	...
14	617	836	I	843	Yes	93	Jul-99	8.3	257	291	ND	ND	Unknown	GN2 & water Mo	OV 102 OMDP	...
15	627	831	I	832	Yes	93	Jul-99	8.3	3785	636	ND	ND	Unknown	GN2 & water Mo	OV 102 OMDP	...

[a] Proud height (height of PTFE seal inner diameter above downstream bleed port metal) inferred from pilot poppet versus armature travel

Abbreviations used: ··· = *not applicable*; ATP = *acceptance test procedure*; C=circumferential, HPF=high pressure forward, GN2=gaseous nitrogen, IFA=in-flight anomaly, ID = inner diameter, I=intermittent, Met.=Metrology, Mo=main valve opening time, Mc=main valve closing time, ND = not determined; OD = outer diameter, OMDP = Orbiter Maintenance Down Period; OV = Orbiter Vehicle; PLT=poppet lift test, PM = preventative maintenance; R&R=replacement and repair, Space Transportation System Flight, S/N = serial number

Table 2

Known and Suspected Type I and Type II Extrusion Cases Detected During Ground ATP through 2003

Case No.	Thruster S/N	Fuel Valve S/N	Fu vlv Retainer Type	Ox Valve S/N	Ox vlv GHe leakage out-of-spec at time of Fu vlv R&R	Last STS	Last Mission Date	Years in Service	Burns	Ontime (s)	Seal ID Height (in.)	Seal OD Height (in.)	Extrusion Type	Basis for Extrusion	Why Pulled?
Ground Failures (Known Type)															
1	137	609	C	753	No	112	Oct-02	18.6	4396	1579	0.0041	0.0102	Type I	GN2 Mo, Met	Coating Chip, PM flush
2	202	229	C	250	Yes	110	Apr-02	14.6	483	488	0.0082	0.0106	Type I	GN2 & water Mo, Met	PM flush
3	217	508	C	794	Yes	86	Sep-97	16.0	1532	720	0.0081	0.0143	Type I	GN2 & water Mo, Met	OV 104 OMDP
4	223	548	I	537	No	76	Mar-96	7.2	128	82	0.0047	0.0129	Type I	water Mo, PLT, Met	PM flush - manifold
5	227	681	C	734	Yes	86	Sep-97	8.9	114	29	0.0084	0.0137	Type I	GN2 Mo, PLT, Met	OV 104 OMDP
6	228	724	I	752	Yes	95	Oct-98	8.3	9221	1432	0.0078	0.0115	Type I	GN2 Mo, Met	PM flush - manifold
7	305	710	I	274	Yes	83	Apr-97	8.7	938	320	0.0045	ND	Type I	GN2 Mo, PLT	PM flush - Grnd Lk
8	325	553	I	251	No	80	Nov-96	1.7	2976	500	0.0041	0.0082	Type I	GN2 Mo, Met	OV 105 OMDP
9	327	580	C	605	No	77	May-96	13.0	5648	1107	0.0076	0.0119	Type I	water Mo, Met	PM flush - Grnd Lk
10	331	544	C	720	No	63	Feb-95	10.6	2856	979	0.0065	ND	Type I	GN2 Mo, PLT	PM flush - Grnd Lk
11	331	718	I	720	No	86	Sep-97	2.4	78	61	0.0057	0.0142	Type I	GN2 Mo, Met	OV 104 OMDP
12	337	594	C	602	Yes	80	Nov-96	12.9	2014	962	0.0035	ND	Type I	GN2 & water Mo, PLT	OV 105 OMDP
13	420	578	C	758	No	105	Aug-01	16.4	1688	254	0.0041	0.0095	Type I	water Mo, Met	PM flush
14	424	273	C	660	No	108	Dec-01	16.7	5233	1003	0.0074	0.0123	Type I	GN2 Mo, Met	PM flush - manifold
15	428	711	I	550	No	105	Aug-01	13.2	1555	371	0.0050	0.0043	Type I	water Mo, Met	PM flush
16	432	622	C	542	No	70	Jul-95	10.5	2994	1011	0.0070	ND	Type I	water Mo, PLT	OV 103 OMDP
17	434	642	C	756	No	105	Aug-01	16.4	2263	873	0.0046	0.0098	Type I	water Mo, Met	PM flush
18	461	546	C	554	Yes	105	Aug-01	13.4	1634	816	0.0044	0.0100	Type I	GN2 Mo, Met	OV 103 OMDP
19	476	716	I	703	No	105	Aug-01	4.9	433	150	0.0056	00098	Type I	GN2 Mo, Met	Exceeded allowable ΔP
20	497	744	I	741	Yes	63	Feb-95	5.8	5252	1008	0.0055	ND	Type I	Met	Control (R.I. Downey
21	571	893	I	785	Yes	77	May-96	5.2	3147	477	0.0065	0.0090	Type I	GN2 Mo, Met	OV 105 OMDP
22	601	806	I	803	Yes	77	May-96	5.7	145	68	0.0070	0.0139	Type I	GN2 Mo, Met	OV 105 OMDP
23	603	803	I	806	No	77	May-96	5.7	637	310	0.0045	ND	Type I	GN2 Mo, PLT	OV 105 OMDP
24	108	679	C	622	Yes	70	Jul-95	7.6	2614	456	0.0020	0.0100	Type II	GN2 Mo, Met	OV 103 OMDP
25	125	604	C	731	Yes	76	Mar-96	12.1	4476	993	0.0011	0.0091	Type II	GN2 Mo, Met	PM flush - manifold
26	126	263	C	773	No	77	May-96	15.7	1109	249	0.0017	0.0061	Type II	GN2 & water Mo, Met	OV 105 OMDP
27	205	538	C	674	Yes	108	Dec-01	20.2	1850	511	0.0013	0.0074	Type II	GN2 Mo, Met	PM flush
28	229	552	C	724	No	86	Sep-97	14.7	4193	770	0.0000	ND	Type II	GN2 Mo, PLT	OV 104 OMDP
29	237	543	C	534	No	86	Sep-97	15.9	1249	418	0.0000	ND	Type II	GN2 Mo, PLT	OV 104 OMDP
30	317	584	C	597	Yes	86	Sep-97	13.8	1515	1373	0.0025	ND	Type II	GN2 Mo, PLT	OV 104 OMDP
31	318	571	C	588	Yes	67	Mar-95	11.1	1696	945	0.0025	0.0087	Type II	Met, water Mo	RP01 Fire at KSC
32	332	569	C	584	No	86	Sep-97	13.4	1230	608	0.0000	ND	Type II	GN2 Mc, PLT	OV 104 OMDP
33	335	575	C	587	Yes	70	Jul-95	11.1	5659	1719	0.0000	ND	Type II	GN2 Mo, PLT	OV 103 OMDP
34	411	637	C	634	Yes	81	Jan-97	13.9	2181	736	0.0017	0.0101	Type II	GN2 & water Mo, Met	PM flush - manifold
35	421	582	C	714	Yes	80	Nov-96	13.8	3791	725	0.0012	0.0096	Type II	GN2 Mo, Met	OV 105 OMDP
36	422	586	C	629	Yes	77	May-96	11.7	205	163	0.0000	ND	Type II	PLT	OV 105 OMDP
37	437	600	C	598	Yes	81	Jan-97	13.1	1702	655	0.0000	ND	Type II	GN2 Mo, PLT	PM flush - manifold

Abbreviations used: amb.=ambient, C=circumferential, HPF=high pressure forward, GHe = gaseous helium, GN2=gaseous nitrogen, IFA=in-flight anomaly, ID = inner diameter, I=intermittent, LT=low temperature, Met.=Metrology, Mo=main valve opening time, Mc=main valve closing time, NDL=no detectable leakage, OMDP=Orbiter Maintenance Down Period, OD = outer diameter, PM=preventative maintenance flush PLT=poppet lift test, R&R=replacement and repair, Space Transportation System Flight, scch = standard cubic centimeters per hour.

allowed the years in service,[##] number of burns, cumulative ontime, average time per burn, adjacent oxidizer valve R&R history to be determined for any given fuel valve. Vacuum bakeout and cover cap epoxy cure histories were obtained from the WSTF Chamber Lab and WSTF Depot, respectively.

Gaseous helium (GHe) leakage data (only high pressure forward leak rates at ambient temperature are considered in this paper) were taken from WSTF-issued TT&E (*Test Teardown and Evaluation*) reports. The dependence of extrusion on thruster duty cycle (firing priority, duration, and sequence during mission) was not investigated. The effect of heat soakback during post-ATP hot fire tests was also not investigated; however, temperatures rarely exceed 60 °C (140 °F), if ever, even after steady state burns on-ground.[***] The possible effect of solar (attitude) heating is discussed elsewhere.[8]

Analytical Methods

A Haake-Fisons (formerly Seiko) Model 120C Thermomechanical Analyzer equipped with a liquid nitrogen cooling accessory was used to measure the instantaneous and permanent extrusion of a pilot seal from a pilot seat assembly. To accommodate as-received pilot seat assemblies (TMA quartz sample holder diameter = 0.39 in. (10 mm)), excess metal from the pilot seat assembly was removed by machining with isopropyl alcohol, thus avoiding frictional heating. The effect of thermal cycling was evaluated by heating the machined parts to temperatures ranging from 52 °C (125 °F) to 93 °C (200 °F).

A Nicolet Magna 750 single beam instrument with a Spectra-Tech Model 0047-009 microscope attachment equipped with a Mercury Cadmium Telluride (MCT/B) detector was used for qualitative infrared identification. FORP analyses were performed either by direct transfer of a small amount of residue to a zinc selenide window, which was then analyzed in transmission mode, or directly transferred to a diamond cell, which was then compressed and analyzed with the FTIR microscope. In general, 64 scans were collected at a resolution of 2 cm^{-1}. Diamond cell window spacings were used at a compression level that minimized interference patterns in the spectrum. Spectral matches were obtained by comparing spectra with those in a WSTF materials library and the Aldrich Condensed Phase library.

The presence of energetic propellant species, i.e., FORP, in PTFE pilot seals was evaluated using a TA Instruments Model 2920 Differential Scanning Calorimetry (DSC) in accordance with procedures given in ASTM Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis (D 3418) (both first and second heating curves were used). Care was taken to sample material at the sealing interface (leg) in addition to material from the recessed cavity (foot). All samples (10 mg) were equilibrated at 40 °C, then heated at 10 °C min^{-1} from 40 to 380 °C with an isothermal dwell of 10 min at 380 °C, cooled to 40 °C at 10 °C min^{-1}, equilibrated at 40 °C, then followed by the second heating. All determinations were conducted under nitrogen.

Following removal of the retainer, visible FORP residues on the exposed PTFE and C455 surfaces, were sampled and analyzed for ammonium [NH_4^+], methylammonium [$CH_3NH_3^+$], and dimethylammonium [$(CH_3)_2NH_3^+$]) using a Dionex DX-600 Ion Chromatograph (IC) system equipped with a cation exchange column in conjunction with conductimetric detection. Residues were also analyzed for hydrazinium [$NH_2NH_3^+$], monomethylhydrazinium [$CH_3NH_2^+NH_2$] and unsymmetrical-dimethylhydrazinium [$(CH_3)_2NH^+NH_2$] using a Hewlett-Packard Model 1100 High Performance Liquid Chromatograph (HPLC) equipped with an ion exchange column in conjunction with amperometric detection. Nitrate (NO_3^-) analyses were performed using a Dionex DX-600 Ion Chromatograph (IC) system equipped with an anion exchange column in conjunction with conductimetric detection. When sufficient residue was available, every attempt was made to determine the amount and stoichiometry of FORP species present.

Specific gravity (density) of PTFE pilot seals was determined in accordance with ASTM Test Method for Specific Gravity of Plastics by Displacement (D 792) and weight percent crystallinity, W^c, determined by measuring the density of as-received rod stock (ρ) and using literature values for densities of the pure amorphous (ρ_a) and pure crystalline (ρ_c) phases[9] according to the relationship:

$$W^c = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \times 100\% \qquad (2)$$

The apparatus used was a Mettler AT201 analytical balance and Mettler Toledo Density Determination Kit for AT balances. Samples were allowed to sit in

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[##] The number of years in service for each valve was based on thruster installation and removal dates, instead of thruster shipping dates from the manufacturer or repair facility, or pod-on and pod-off dates at KSC.

[***] Meersheidt, M., Private communication. White Sands Test Facility, Las Cruces, New Mexico. May 2003.

the lab for 24 hours prior to testing at 23 ± 2 °C at ambient humidity. The submersion medium used was boiled, deionized 18 MΩ cm water. After boiling, 1-2 drops of Zonyl®[†††] fluorosurfactant wetting agent was added per 100 mL water. A magnifying glass was used to further insure no air bubbles clung to submerged parts during weighings.

The magnitude and type of extrusion was determined by making impression replicas of the sealing interface of Marquardt P/N 235681. Replicas were made from Reprorubber Thin Pour #16135 (FlexBar Machine Corp., Islandia, NY). After curing, the replicas were sectioned, and seal heights were measured in at two locations 180° apart using a Leco 300 Metallograph equipped with a Mitutoyo Model ID-C125EB precision x-y recorder with 1-0.00005 in. (25.4-0.0001 mm) resolution. All pilot seal height measurements were made at 32 to 63× magnification under polarized light.

Calculations

The extrusion volume was approximated as π {*id* height·$[r_{poppet}^2 - r_{id}^2]$ + *od* height·$[r_{od}^2 - r_{poppet}^2]$} where *id* and *od* heights were determined by impression replica metrology; and r_{od}, r_{id}, and r_{poppet} were midrange tolerances taken from engineering drawings. The maximum extrusion due to complete stress relief of a pilot seal after interference fitting was calculated using mid-range design tolerances for mating PTFE and metal parts. For example, the pre-installation volume of the PTFE pilot seal preform was calculated as:

$$V_{preform} = \int_{r_{id}}^{r_{ood}} (h_{seal}(r) - h_{nonseal}(r))2\pi r dr \quad (3)$$

where r_{id} was the inner diameter of the exposed sealing surface, r_{ood} was the outer diameter of the entrapped nonsealing surface, and h_{seal} and $h_{nonseal}$ were radially dependent functions describing the 8°-angled sealing surface, and outer diameter of the entrapped nonsealing interface, respectively. Both h_{seal} and $h_{nonseal}$ were modified to account for corner radii and edge breaks. A similar expression was derived for the metal cavity volume, $V_{cavity,}$, allowing calculation of the interference fit (or overfill = ΔV (=V_{seal}-V_{cavity}). This allowed the maximum allowable *id* and *od* extrusion, Δl_{id} and Δl_{od}, due to stress relief to be calculated as:

$$\Delta l_{id} = \frac{\Delta V_{id}}{\pi\left(r_{poppet}^2 - r_{id}^2\right)} \text{ and, } \Delta l_{od} = \frac{\Delta V_{od}}{\pi\left(r_{od}^2 - r_{popppet}^2\right)} \quad (4)$$

where $\Delta V_{id} + \Delta V_{od} = \Delta V$. All dimensions corresponded to midrange (nominal) tolerances taken from respective Marquardt engineering drawings for the seat (drawing 235677 Rev. E), preform (drawing 234161, Rev. F), and retainer (drawings 234160 Rev. D for circumferentially-welded (C-welded) retainers, and 235679 Rev. B for intermittently-welded (I-welded) retainers).

RESULTS & DISCUSSION

Thermal Cycling of Flight-like Pilot Seat Assemblies

Pilot seals undergo extensive thermal cycling throughout their service lifetime. For example, during routine thruster flushing with water and nonroutine valve removal and replacement (R&R), thrusters or valves removed from thrusters are subjected to 1.5 to 8-hr vacuum bakeouts at 54 to 77 °C (130 to 170 °F).[‡‡‡] Also, the cover cap on the valve body must be periodically recoated with epoxy which requires curing at 90 ± 5 °C (194 ± 9 °F) for 1 hr, entailing heating of the valve body, and, consequently, the pilot seal. During mission, operational temperatures as high as 69 °C (157 °F) are allowed by flight rules; however, non-operational temperatures as high as 100 °C (212 °F) may be encountered during descent (especially for the forward downward firing thrusters).

To evaluate the effect of thermal cycling on extrusion, new pilot seat assemblies were cycled in a TMA furnace to 60 °C (140 °F). After three cycles ~4 microns (0.2 mil) of pilot seal *od* extrusion was produced (Figure 4). The amount of recovery (return to the original dimension) was nearly quantitative after the second and subsequent heatings. Subsequent heatings to higher temperatures produced more extrusion, again with time-dependent recovery noted between heatings (data not shown). Similarly, thermal cycling of an unextruded oxidizer valve pilot seal to 80 °C (175 °F) produced ~7 microns (0.3 mil) of *od* extrusion (data not shown), again with nearly quantitative recovery after the second and subsequent heatings.

The average *od* extrusion observed for extruded fuel valve pilot seals taken from the field was

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[†††] Zonyl® is a registered trademark of E. I. DuPont and Nemours and Company., Wilmington, DE.

[‡‡‡] In-house documents. *PRCS Thruster Flush Procedure.*, WJI-PROP-CTF-0010.D, Issued Sept. 17, 1999; and *WSTF PRCS Thruster Valve Overhaul and Repair – Valve Acceptance Test Procedure.*, WJI-PROP-CTF-0018.D, Issued Sept. 26, 1999, NASA Johnson Space Center White Sands Test Facility, Las Cruces, New Mexico.

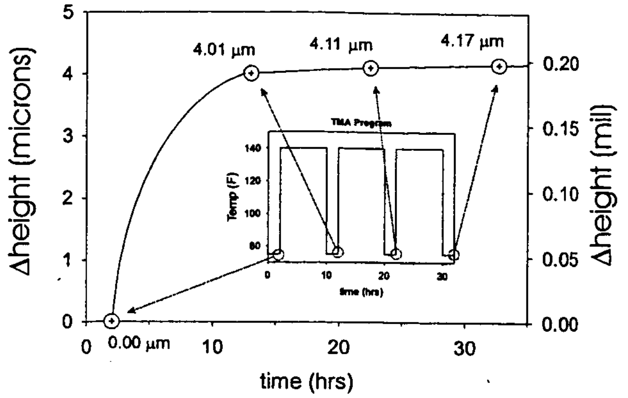

Figure 4 Thermomechanical analysis data showing incremental extrusion of a pilot seal after three consecutive 8-hr. excursions to 60 °C (140 °F) under conditions of negligible sealing load.

211 ± 102 μm (8.3 ± 4.0 mil, n=35).[§§§] Therefore, the TMA data suggest that factors other than thermal cycling contribute to extrusion. However, it must be noted that the load on the pilot seal during TMA (0.098 N (0.022 lb$_f$)) was negligible compared to the load in service due to poppet spring-loading and liquid propellant system pressure (25 N (5.6 lb$_f$)). In fact, the load in service is large enough to cause *ca.* 20 percent lateral cold flow[¶¶¶] of the PTFE, leading to 'mushrooming' of the PTFE outside of the metal cavity. It is proposed herein that the resulting excess plug of PTFE outside of the pilot seal cavity effectively hinders recovery of the pilot seal after heating, leading to more extrusion than shown in Figure 4.

More realistic data evaluating the effect of thermal cycling under conditions duplicating poppet spring-loading and liquid propellant system pressure were obtained during component-level exposure tests conducted at WSTF.[10] Six consecutive ground turnaround-mission profiles were simulated, including worst case saturated oxidizer vapor exposures on-ground, and mission descent heatings to 100 °C (212 °F). Post-test metrology revealed 58 ± 13 μm (2.3 ± 0.5 mil, n=2) of *od* extrusion, short of the 211 μm value observed in the field. However, if the exposure test had been continued for 16.8 missions (the average number of missions for the 68 extrusion cases cited in this paper), linear extrapolation would predict 161 ± 36 μm (6.3 ± 1.4 mil) of *od* extrusion, which approaches the 211 μm value observed in the field.

What balance of extrusion remains could be due to thermal cycling from other heat sources not simulated in the exposure tests (such as solar heating, vacuum bake-outs, epoxy cures, and ground firings). The possible effect of increased lateral cold-flow in the field due to valve actuation (actuation ⇒ increased cold flow ⇒ less recovery ⇒ more extrusion) was also considered. Unactuated propellant-exposed (fuel + oxidizer) pilot seals used in the component-level exposure test, exhibited 13 percent lateral cold-flow ($r_{od} - r_{id}$ = 691 ± 17 μm (27.3 ± 0.7 mil), n=2), which approaches the 20 percent value observed for extruded pilot seals taken from the field.[¶¶¶] By comparison, unactuated fuel-exposed pilot seals exhibited negligible lateral cold-flow ($r_{od} - r_{id}$ = 643 ± 3 μm, (25.3± 0.1 mil), n=2). This suggests that static poppet load (without actuation) in the presence of oxidizer vapor is sufficient to cause significant lateral cold flow. It is therefore plausible that oxidizer vapor can contribute to extrusion in two distinct ways: 1) reversible uptake of oxidizer and subsequent disruption of intramolecular attractive forces, causing in turn softening and increased lateral cold flow, thereby preventing seal recovery, and 2) irreversible de-densification and increased compressibility caused by reaction of oxidizer with fuel inside the bulk PTFE (*vide infra*).

Service History Correlation

Correlation with Mission Firing Histories

A review of service history records revealed an apparent link between extrusion type and years in service. For example, verified Type II cases have, on average, logged more years in service (13.5 ± 3.9 years, n = 7), than verified Type I extrusion cases (9.8 ± 5.2 years, n = 31) (Figure 5).[###] Similarly, Type I extrusion cases had, on average, fewer burns and lower mission ontime than Type II cases. This suggests that cumulative load at temperature and the number of valve actuations during firing are important determining factors of extrusion type. Interestingly, all ten extrusion-related IFAs exhibit Type I extrusion, a majority of those (8 of 10 cases) failed with unusually low burns, ontime, and years in

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[§§§] Note: *od* extrusion = final *od* height – initial *od* height (initial *od* heights were generally not known, but based on mid-range engineering tolerances, would have a value of 99 and 124 μm (3.9 and 4.9 mil) for circumferentially and intermittently-welded pilot seats assemblies, respectively.

[¶¶¶] The amount of lateral cold flow, given by $r_{od} - r_{id}$, of representative, actuated, extruded pilot seals was found to be 781 ± 22 μm (30.7 ± 0.9 mil, n = 5), compared to 641 μm (25.3 mil) midrange tolerance for a starting pilot seal perform.

[###] Only cases in which extrusion type was verified by impression replicas were considered.

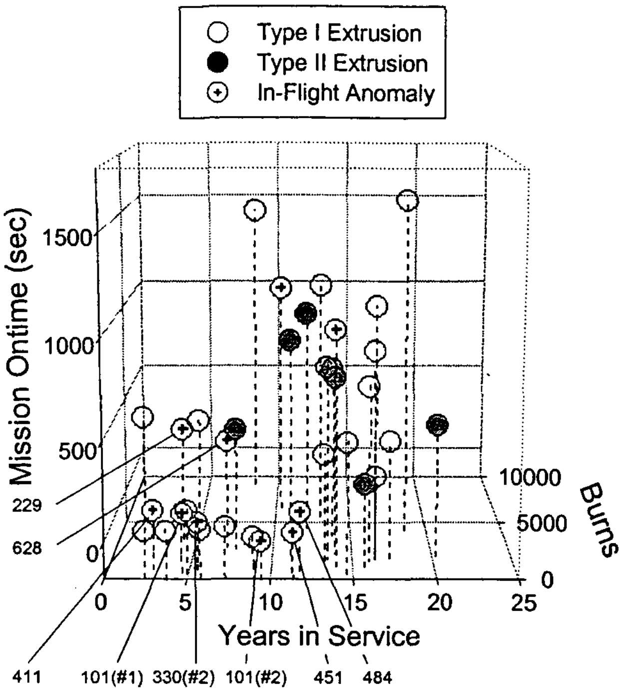

Figure 5 Distribution of extrusion type with selected service history parameters for thrusters of verified extrusion type (based on metrology data).

service. These may be considered to have failed prematurely (see Figure 5, thrusters 101 #1, 101 #2, 229, 330, 411, 451, 484, and 628).

Slightly more than the expected number of aft reaction control subsystem (ARCS) versus forward reaction control subsystem (FRCS) extrusion cases was observed (49 of 68 cases or 72 percent of extrusion cases came from ARCS thrusters, versus 28 of 38 thrusters or 63 percent expected). It is unclear if the higher than expected ARSC:FRSC failure ratio is related to duty cycle (e.g., aft steady state burns for delta V maneuvers) or statistical scatter. No correlation ($R^2 = 0.09$) was found between the amount of extrusion and the number of missions, which varied from 5 to 27 missions for the 68 extrusion cases cited in this paper.

Inspection of mission usage patterns since 1991 (approximate UTPA installation date, STS-37 on) showed that extrusion has occurred in all 24 aft firing locations, and in 9 of the 14 forward firing positions (extrusion absent in F1U, F2U, F1L, F2R, and F2D). There was also a *slightly* greater incidence of extrusion in downward firing ARCS thrusters, and in forward firing FRCS thrusters; however, it is presently unknown if these apparent trends stem from position-specific GN_2 trickle purge effectiveness, mission duty cycle, or statistical scatter.

Correlation between the amount of extrusion and various mission service history parameters (number of years in service, burns, ontime, and time per burns since installation) were generally poor; however, a plot of the amount of extrusion against years in service gave a R^2 of 0.54 for Type II extrusion cases (plot not shown). (By comparison a plot of the amount of extrusion against years in service gave a R^2 of 0.09 for Type I extrusion cases.) This suggests that years in service may have some influence on Type II extrusion. Similarly, correlations between specific service history parameters were poor; however, a plot of the time per burn against the number of burns on-orbit gave a R^2 of 0.36 for Type II extrusion cases (plot not shown). This suggests that longer burns may contribute to the reduction of valve life as measured by the number of burns, and again augments the notion that only Type II extrusion cases show any dependence on service history. Last, the service histories of active fuel valves (without extrusion) were found to overlap those of failed fuel valves (with extrusion).

Correlation with Vacuum Bakeout and Epoxy Cure Histories

To determine if thermal cycling from non-mission related (ground) heat sources contributing to extrusion, WSTF vacuum bakeout records for the period January 1995 to May 1997 were examined, along with epoxy cures records for the period March 1996 to January 2002. For thrusters processed at WSTF before or after the 1995-1997 interval, bakeout times were estimated.[****] Results show that cumulative vacuum bakeout times were on average greater for active OEM fuel valves (31.4 ● 6.2 hr, n = 104) than OEM fuel valves that failed due to extrusion (20.2 ± 11.7 hr, n = 47). Therefore, there is little basis to link vacuum bakeouts performed at WSTF with extrusion. It was also determined that active and failed OEM fuel valves were returned to Marquardt and WSTF for thruster processing at about the same rate (Table 3). Therefore, there is little basis to link earlier bakeouts performed at Marquardt with extrusion either.

Examination of epoxy cover coat curing records showed that of the seventy-nine unique PRCS valves or thrusters that received an epoxy cure during the 1996 to 2002 period, 19 were fuel valves, 29 were oxidizer valves, and 31 were thrusters (fuel and oxidizer valves). Of the 50 (19+31) fuel valves that received an epoxy cure, only 2 subsequently failed due to extrusion (fuel valve S/Ns 714 and 642 on

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[****] 9.5 h at 55 +10 −5 °C (130 +20 −10 °F)) was assumed for thruster flushes; an additional 27 h at 55 +10 −5 °C (130 +20 −10 °F)) was assumed for valve R&Rs.

Table 3
Average Number of Returns to Repair Agencies for Thrusters with Active versus Failed (Extruded) Fuel Valves

	Avg. No. of Returns	
Agency	Active	Failed
Marquardt	0.7 (0.8)	0.8 (0.8)
WSTF	2.0 (0.9)	1.8 (0.7)

NOTE: Numbers in parentheses are standard deviations.

Table 4
Gaseous Helium Leakage Rates for Oxidizer Valves Next to Active and Failed (Extruded) Fuel Valves

	Number of Returns	None 0 scch	Low 1-99 scch	Medium 100-350 scch	High >350 scch
Active	244	140	23	17	64
		(57)	(9)	(7)	(26)
Failed	80	12	14	15	39
		(15)	(18)	(19)	(49)

NOTE: Numbers in parentheses are percentages; scch = standard cubic centimeter per hour

thruster S/Ns 332 and 642, respectively). Since this failure rate (2 failures out of 50 epoxy cures, or 4 percent) is much less than the overall extrusion failure rate from 1994 to 2003 (68 failures out of 283 returns, or 24 percent), there is little basis to link epoxy cures with extrusion.

Correlation with Oxidizer Valve Failures

As was noted earlier, since 1981, twice as many (220) oxidizer valves have failed than fuel valves (110). The predominant mode of oxidizer valve failure has been leakage, whether manifested as actual oxidizer leakage during mission and ground turnaround at KSC, or GHe leakage during thruster processing at Marquardt or WSTF. Earlier studies have implicated oxidizer leakage as a factor in fuel valve pilot seal extrusion.[7] A higher incidence of concurrent oxidizer valve failure might therefore be expected for extrusion cases. However, a comparison of R&R histories showed a *lower* incidence of concurrent oxidizer valve failure at the time extrusion was detected (41 of 68 cases, or 60 percent), than during nonextrusion-related fuel valve failures detected during 1981 to 1993 (29 of 42 cases, or 69 percent). However, this comparison was based on noncontemporaneous valves processed by different agencies, and thus may be flawed.

Correlation with Oxidizer Valve Leakage

The possible link between extrusion and oxidizer valve leakage (as measured by GHe leakage) occurring since 1994 was then examined (for contemporaneous valves processed by a single agency). Despite known difficulties correlating oxidizer leakage with GHe leakage,[11] evaluation of GHe leakage data was nevertheless revealing (Table 4). Thrusters with active fuel valves were more likely to be next to oxidizer valves with no detectable GHe leakage (NDL) (57 percent or returns) than thrusters suffering from extrusion (15 percent). Active fuel valves were correspondingly less likely to be next to oxidizer valves with excessive (> 350 scch (standard cubic centimeters per hour)) GHe leakage (26 percent), compared to thrusters exhibiting extrusion (49 percent). These observations suggest extrusion is linked to high GHe leakage, and therefore to oxidizer leakage during KSC ground turnaround.

Of the 68 extrusion cases cited in this paper, only 2 lacked any documentation of measurable post-UTPA WSTF GHe leakage or KSC ground oxidizer leakage (fuel valve S/Ns 530 on Thruster 325, and 543 on Thruster 237). However, subsequent investigation showed that fuel valve S/N 543 had 57 desiccant tube change-outs, indicative of high oxidizer valve leakage, during the STS-86, 81, and -76 flows (1, 3 and 5 missions before failure, respectively).[****] By comparison, fuel valve S/N 530 had 7 desiccant tube change-outs during the STS-42 flow (4 missions before failure), but no desiccant tube change-outs were recorded during the STS-68 flow (immediately before failure).

Real time monitoring of thruster chamber oxidizer vapor concentrations at KSC shows that high concentrations (> 100 ppm) can occur despite indications of NDL (GHe) during the previous returns to WSTF.[12] For example, of the ten highest chamber concentrations measured on *Atlantis* during the summer of 2003, six corresponded to oxidizer valves that gave no detectable GHe leakage at WSTF Depot during the previous return. For these reasons, lack of GHe data, or indications of low of NDL GHe leakage, or a low number of desiccant tube change outs, should not be taken as evidence of acceptable or benign levels of oxidizer leakage.

[****] A review of STS-42, -63, -67, -68, 70, -72, 72, -76, -77, -80, -81, -86, and -91 shuttle flow desiccant tube change out data revealed that on average 3.4 desiccant tube change-out are expected for a given thruster per Shuttle flow.

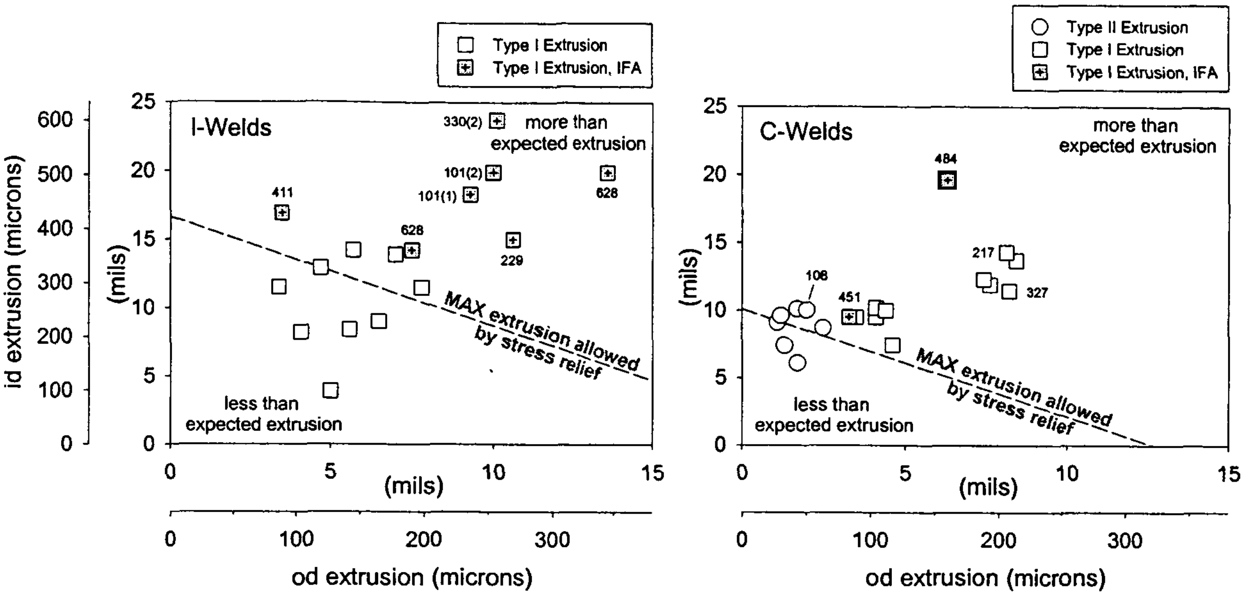

Figure 6 Distribution of intermittently (left) and circumferentially-welded (right) extrusion cases showing observed (symbols) versus expected (dashed lines) extrusion due to stress relief of the PTFE pilot seal.

Extrusion Volume Calculations

The calculated amount of interference fit (overfill) for PRCS POV pilot seals varies from 5.0 to 8.3 percent for C- and I-welded designs, respectively (based on mid-range engineering tolerances). The primary reason for the greater overfill for I-welded designs was a reduction in the metal retainer *id* (at the pilot seal *od* interface) from 4.15 to 4.05 mm (0.1635 to 0.1595 in.). The corresponding metal cavity volumes for the C- and I-welded designs were 20.65 and 20.29 mm^3 (0.001238 and 0.001260 in.^{3}), which translates to as-fabricated overfill volumes of 1.03 and 1.70 mm^3 ($6.3 \cdot 10^{-5}$ in.^{3} and $1.04 \cdot 10^{-4}$ in.^{3}), respectively. Assuming no stress relief occurs during fabrication (worst case), the overfill corresponds to the maximum possible extrusion volume that could occur upon stress relief in service under the condition of conservation of PTFE density.

Examination of extruded pilot seals that failed in service gave extruded volumes as high as 2.85 mm^3 ($1.74 \cdot 10^{-4}$ in.^{3}) for I-welded seat assemblies (fuel valve S/N 605 on thruster 330) and 2.52 mm^3 ($1.54 \cdot 10^{-4}$ in.^{3}) for C-welded seat assemblies (fuel valve S/N 749 on thruster 484). These volumes are significantly higher than the amount allowed by stress relief (Figure 6). Furthermore, pilot seals involved in IFAs tended to have the largest od and id extrusion, and exceeded the maximum allowable extrusion due to stress relief in all 10 cases.

Comparison of Figures 5 and 6 shows that premature valve failure is characterized by excessive extrusion above the amount allowed by thermally-induced stress relief. I-welded pilot seat assemblies have a sharper edge break (max = 10 mm (4 mil)) on the metal retainer along the *od* edge of the pilot seal, compared to a smoother, radiused edge on the metal retainer for C-welded pilot seat assemblies (radius = 0.25 to 0.33 mm (10 to 13 mil)). The sharper edge break may impede seal recovery, and therefore accelerate extrusion. This contention is supported by the data in Figure 6. For example, the I-welded cases (Figure 6, left) tended to yield larger amounts of extrusion (2.75 ± 0.97 mm^3 ($1.08 \pm 0.38 \cdot 10^{-4}$ in.^{3})) than the C-welded cases (2.22 ± 0.74 mm^3 ($0.87 \pm 0.29 \cdot 10^{-4}$ in.^{3})) (Figure 6, right), despite having fewer years in service (I-welds: 5.6 ± 2.7 years, C-welds: 8.2 ± 2.6 years, Figure 6 data normalized to 1991).

Tear-Apart Analyses

FTIR and HPLC/IC Data

Although thrusters receive a decontaminating water rinse upon receipt at WSTF Depot, and a water flush to remove nitrate salts during follow-on processing, pilot seat assemblies with extruded pilot seals were found to give detectable Interscan®[††††] readings several years after valve R&R. Inspection of the pilot seals under magnification (up to 100×)

[††††] Interscan® is a registered tradename of Interscan Corporation, Chatsworth, CA. Interscans are primarily used to monitor hydrazine fuel vapor concentrations, and also respond to FORP.

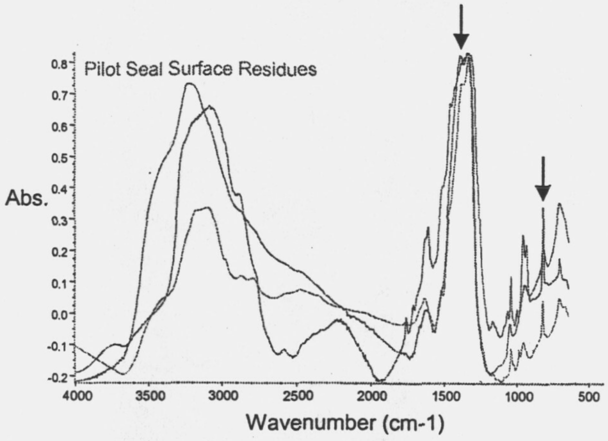

Figure 7 Representative FTIR spectra of FORP residues found on extruded pilot seals from 3 different fuel valves (arrows point to characteristic nitrate absorbances)

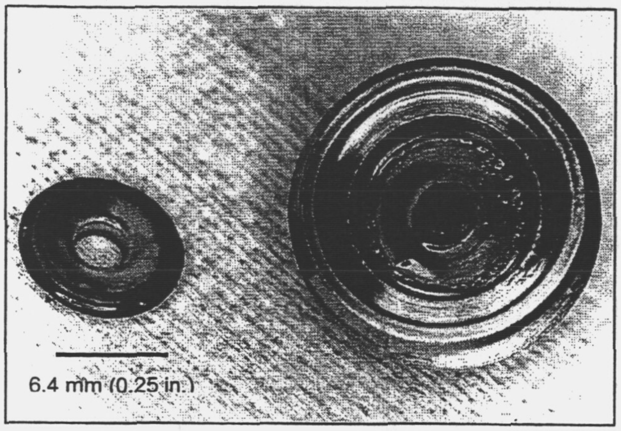

Figure 8 PRCS thruster S/N 217 pilot seat assembly with the retainer and pilot seal removed showing a large quantity of FORP inside the pilot seal cavity.

sometimes revealed the presence of brownish residues on the external pilot seal surfaces, or along the pilot seal *id* or *od*, suggesting post-process blooming or migration had occurred. The FTIR spectra of residues varied slightly, indicative of some compositional variation, however, all spectra were consistent with identification of the residue as FORP. One of the more notable features in the spectra were absorbances at 1383 (very strong) and 835 cm^{-1} (medium), indicative of nitrate anion (Figure 7). Removal of retainers to expose the interior (entrapped) portions of extruded pilot seals revealed FORP residues inside some, but not all pilot seal cavities (Figure 8). Three cases with substantial amounts of FORP residue inside the pilot seal cavity (Figure 5, thruster S/Ns 108, 217, and 327) also had FORP present on the sealing surface or along the seal *id* or *od*, consistent with blooming or migration of FORP after valve R&R. Attempts to relate the amount of residue found inside to cavity with previous oxidizer/GHe leakage or the amount of extrusion were largely unsuccessful. For example, the corresponding GHe leakage rates at the most recent return for the three seats with the most residue varied widely (S/N 108: 126 scch, S/N 217: 9324 scch, and S/N 327: 17 scch). Also, thruster S/N 330 (2nd failure), which had little or no FORP inside the pilot seal cavity, exhibited the largest amount of *od* extrusion (602 microns (23.7 mil)).

FTIR and HPLC/IC analyses of residues such as those depicted in Figure 7 gave the first known, conclusive identification of nitrate anion *inside* a fuel valve pilot seal cavity. HPLC/IC identified methylammonium nitrate (MAN) as the majority constituent in both internal and external fuel valve FORP residues, with little or no methylhydrazinium nitrate (MHN) present. The observation of MAN-rich FORP suggested an engine firing origin, since steady state burns, or pulse mode burns followed by a significant heating event would both lead to formation of more thermally stable MAN at the expense of the more energetic and thermally labile MHN.[13,14] However, FORP composition is very sensitive to the fuel/oxidizer ratio.[15] The possibility therefore exists that high oxidizer vapor concentrations immediately downstream of the fuel valve pilot seal could promote formation of more MAN at the expense of MHN. It is also possible that the long intervals between last mission service and FORP analysis (typically >1 year) could further perturb MAN:MHN ratios.

The most compelling evidence pointing to an origin other than engine firing was obtained in component-level exposure tests[10] simulating on-ground oxidizer vapor exposure and on-orbit thermal cycling. These tests also yielded brownish FORP residues (external), but in the *absence* of thruster firing. Furthermore, the FORP produced was MAN-rich (resulting MAN:MHN mole percent ratio = 83:17, error = 0.8 percent, n=2). Finally, residues collected from pilot seat cavities of oxidizer valves removed from fleet thrusters gave no indication of MAN or MHN. These observations support the conclusion that the FORP often found in association with extruded pilot seals can be produced by a fuel-oxidizer reaction inside or close to the pilot seal in the absence of thruster firing.

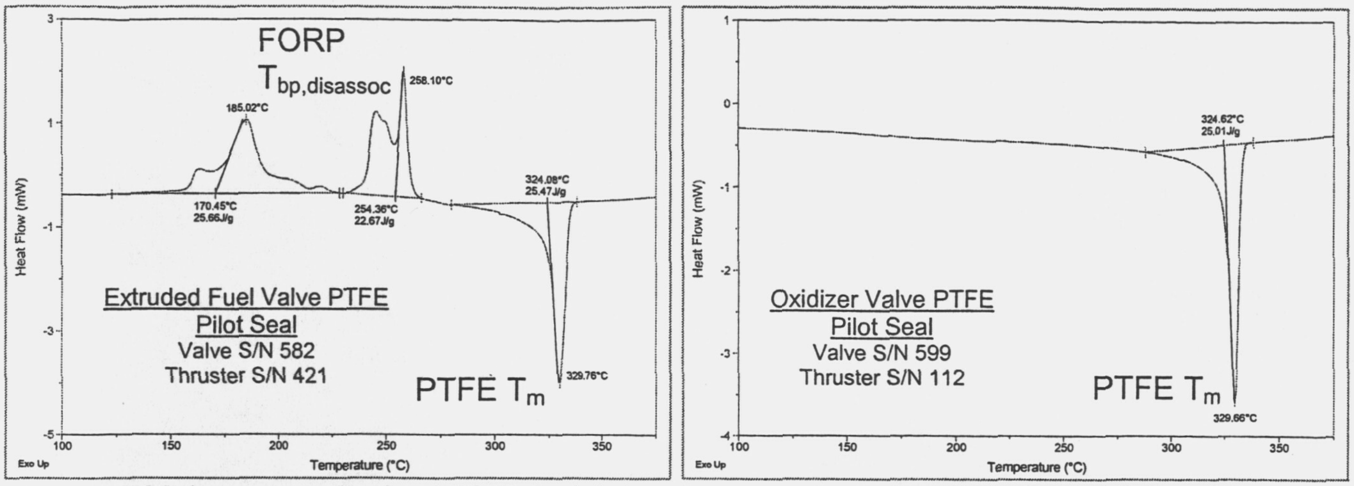

Figure 8 DSC thermograms showing a) FORP that is intimately associated with a fuel valve pilot seal (left), and b) the corresponding lack of FORP observed in conjunction with an oxidizer valve pilot seal (right) (Exo Up).

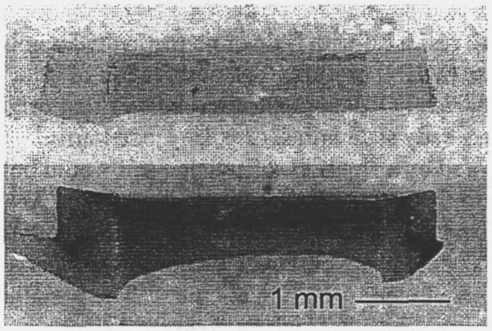

Figure 10 Heat-induced FORP-decomposition resulting in discoloration of a fuel valve pilot seal (valve S/N 254, bottom). An identically heated oxidizer valve pilot seal (valve S/N 599, top) is shown for comparison.

DSC Data

DSC data on extruded fuel valve pilot seals (Figure 9, left) removed from valve S/Ns 254, 508, 553, 582, 672, 718, 764, 893, and 895, showed that FORP was intimately associated with bulk PTFE (i.e., was not removed by previous decontamination, thruster flush, or HPLC/IC rinses. The FORP exotherm to PTFE endotherm peak ratio was 2.2 ± 0.8 (n=9), indicating similar amounts of FORP were associated with the PTFE, regardless of the amount of FORP observed inside the pilot seal cavity. The FORP composition as revealed by the presence of higher (MAN) and lower (MHN) temperature exothermic transitions attributable to FORP melting and/or disassociation, varied from seal to seal, but was uniform about the circumference of a given seal. These exotherms were not apparent during the second heating, indicating the FORP had volatized or disassociated (giving a thermogram similar to that shown in Figure 9, right). Last, the foot of the pilot seal (farthest away from the sealing interface) did not show any exothermic transitions attributable to FORP.

By comparison, unused Teflon 7-A pilot seal preforms and used oxidizer valve pilot seals only exhibit a PTFE melting endotherm at ~330 °C (~625 °F) (Figure 9, right). Extruded fuel valve pilot seals also showed a larger drop in the peak melting temperature between first and second heatings (ΔT_m = 1.5 ± 0.4 °C (2.7 ± 0.7 °F)) than oxidizer valve pilot seals (ΔT_m = 1.1 ± 0.2 °C (2.0 ± 0.4 °F) or unused preforms (ΔT_m = 0.9 ± 0.1 °C (1.6 ± 0.2 °F)). The probably can be attributed to exothermic FORP volatilization and disassociation within the fuel valve pilot seals. Extruded fuel valve pilot seals also were significantly discolored (Figure 10) after heating to 380 °C (715 °F). The discoloration was not superficial, but extended deep into the pilot seal (Figure 9, bottom). By comparison, the unused preforms (not shown) and oxidizer valve pilot seals (Figure 10, top) retained the characteristic white, opaque appearance of PTFE.

Fuel Valve S/N 544 Pilot Seal Failure Analysis

One of the more interesting failure analyses was conducted on the pilot seal from thruster S/N 101 (2nd failure), fuel valve S/N 544 (involved in an IFA on STS-108). Removal of the retainer revealed little or no FORP inside the pilot seal cavity, despite the presence of an oxidizer valve with well-documented history of GHe and oxidizer leakage. Most surprising was the presence of a fracture or void along the pilot seal *od* (Figure 11). This fracture was similar to one

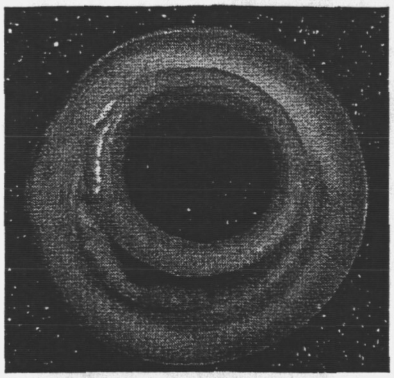

Figure 11 Fracture/void located along the outer diameter (at 7 o'clock) of an extruded pilot seal removed from thruster S/N 101, fuel valve S/N 544. The inner (hole) diameter is 2.8 mm (0.11 in.).

observed in the pilot seal from fuel valve S/N 530 (thruster S/N 325) although that fracture was located along the pilot seal *id.*[7]

Scanning Electron Microscopy (SEM) of the area immediately above the fracture region of the S/N 544 pilot seal revealed axial fissuring, suggesting tensile failure. SEM also revealed the presence of fine scale features immediately above and below the fracture, namely, machining grooves that had been introduced during latheing operations to fashion the preform from bar stock, suggesting the absence of temperatures well in excess of the 330 °C (625 °F) melting point for PTFE. DSC of PTFE cut from fracture area showed no FORP (similar to the thermogram shown in Figure 9, right), in contrast to the previous results obtained on 9 extruded pilot seals that did not exhibit any fracturing.

The two leading explanations for the fracture are 1) origination from a preexisting flaw introduced during fabrication, and 2) occurrence of a highly localized exothermic event involving FORP. A more remote explanation accounting for the lack of FORP could be exposure to high energy (450 keV accelerating potential) radiation during attempts to measure the amount of extrusion by X-ray Computed Tomography.

Specific Gravity

Specific gravity data on extruded pilot seals removed from fleet service showed that extruded seals had significantly lower densities than oxidizer valve pilot seals or unused PTFE pilot seal preforms (Table 5). Extruded pilot seal PTFE density was outside of the allowable 2.14 to 2.20 g cm^{-3} range stipulated for Teflon 7A by the OEM.[16] The resulting de-densification would make the PTFE more compressible than expected under conditions of oxidizer uptake alone, thus exacerbating lateral cold flow and further preventing seal recovery, and leading to more extrusion over shorter periods of time.

Table 5
Pilot Seal Densities

Pilot Seal Type	Density (g cm^{-3})	*n*
Unexposed Preform	2.172 (0.012)	7
Oxidizer-exposed	2.156 (0.008)	2
Fuel-exposed	2.102 (0.017)	5

NOTE: Numbers in parentheses are standard deviations.

SUMMARY

Some extrusion is unavoidable and a natural consequence of using an oversized, semitrapped plastic seal in a thruster application which subjects the seal to thermal cycling. The available data support the conclusion that oxidizer vapor plays a significant contributing role in fuel valve pilot seal extrusion. For example, FTIR, HPLC/IC, DSC, and component-level exposure test data all support the conclusion that FORP produced in the absence of thruster firing becomes intimately associated with the pilot seal and pilot seal cavity during the valve's service lifetime. Oxidizer valve leakage data, specific gravity results, metrology data, and interference fit stress relief calculations all support the conclusion that oxidizer leakage, coupled with a partially effective GN_2 trickle purge, causes reversible and irreversible modification of the PTFE, thereby exacerbating extrusion beyond levels expected to occur in response to thermally-induced stress relief. The available data also suggests that the retainer redesign has worsened the tendency of pilot seals to extrude. The classification of Type I versus Type II extrusion was found to be somewhat arbitrary. Type II cases actually appear to constitute a less severely extruded subset within the Type I family, with distinctions between the two subsets attributable to differences in accumulated service. Last, thrusters failing on-orbit have pilot seals with more severe levels of extrusion than thrusters failing on-ground. The additional extrusion appears to originate from an adverse fuel-oxidizer reaction in or near the pilot seal occurring in the absence of thruster firing.

RECOMMENDATIONS

Towards reducing the incidence of extrusion, several proactive mitigation strategies have been proposed. In general, these strategies involve modification of existing or implementation of new ground processes:

- Implement a more effective trickle purge, with minimal purge downtime.
- Monitor real-time oxidizer vapor concentrations within the thruster chambers during ground turnaround.
- Remove and replace fuel valves that already show signs of extrusion as revealed by current trace or other sensitive diagnostic test data.
- Lower the allowable GHe leakage rate for existing and new oxidizer valves.

Several incremental improvements are also possible. For example, the use of better pilot seal materials-of-construction could make pilot seals less susceptible to 1) propellant uptake subsequent property modification during service , and 2) deformation under load at temperature. Finally, it is generally good practice to precondition softgoods at the anticipated service temperatures immediately before final part finishing, however, this practice was disbanded by the OEM. At present, only the starting rod stock is annealed. For this reason, the recommendation is made to anneal as-welded pilot seats assemblies immediately prior to final pilot seal trimming.

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