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FY99 Status Report on the HSV

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Kirk L. Shanahan

September, 1999

Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808

Prepared for the U.S. Department of Energy under
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Summary

The HSV in storage in MTF has been monitored during FY99, and its overpressure has been sampled and analyzed. The HSV's internal pressure continues to rise slowly, and the overpressure still analyzes as 100% ^{3}He. The titanium tritide sample that was to be monitored annually and which had developed a leak last year has been repaired and isotherms measured. Unfortunately the sample was showing significant unexpected ^{3}He release, so the isotherm data is corrupted by unknown levels of ^{3}He. This release has disqualified this sample for future use, as it is now seriously divergent from the HSV material. A different sample must be selected for subsequent studies.

The unexpected ^{3}He releases of the Ti-3 sample and the possible release in other Ti samples have raised a serious issue. It should be determined why this release is occurring, so that an unexpected release of ^{3}He during HSV unloading can be assessed as unlikely.

Part 1. The Hydrogen Storage Vessel

The first loaded HSV, HSV-002, was loaded on April 3, 1996 and delivered to the MTF where it was installed on a monitoring manifold. The HSV's temperature and pressure have been monitored since that time. A plot of the raw pressure data is shown in Figure 1. (In the FY97 report, the pressure data was reduced to a common temperature also, but this procedure did not produce an significant improvement, so it is not done here.)

In general, a linear increase in pressure is observed with time. However, a change in slope is noted at approximately day 1050, just after the Baratron pressure sensor was replaced. Unfortunately, the point where the change would have first been noted was obscured in the region where the installed Baratron was malfunctioning.

Both regions of the pressure vs. time curve are well fit by a straight line. The early data, ignoring the first few points that fall off the line, are fit with an equation:

$$\text{Pressure} = 0.0156 * \text{day} + 12.4 \quad R^2 = .998 \quad \sigma = 0.16$$

The later data set is fit with:

$$\text{Pressure} = 0.0467 * \text{Day} - 18.1 \quad R^2 = .987 \quad \sigma = 0.30$$

This implies the rate of pressure increase has increased from about 16 millitorr per day to about 47 millitorr per day, about a factor of three increase. The intercept point of these two lines is day 981.

The HSV design parameters that are used to indicate a possible problem are if the pressure reaches 500 psi, or the generation rate exceeds 7%. It would take over 1500 years at the current generation rate to reach 500 psi. The amount of gas still represents much less than 1% of the total ^{3}He produced by decay inside the HSV. The overpressure sample was analyzed and contains 99.51% ^{3}He, with 0.25% of all three hydrogen isotopes detected.

The plot has two problem points indicated. The first is a period where no monitoring was possible due to a thermocouple vacuum gauge failure during overpressure sampling. Due to the sampling procedure, the HSV had to remain valved off from the manifold while the TCVG was replaced.

The second problem point occurred when a steam outage in building 232-H produced condensation on HVAC ducts. Which then dripped into the Baratron pressure sensor's electronics unit. This has apparently caused both an increase in noise level and a baseline shift. The Baratron was replaced on day 1044 (Feb. 11, 1999). This region is marked "Suspect Data" on Figure 1.

Part 2. The Titanium Tritide Samples

Nine titanium tritide samples were originally prepared with varying tritium and deuterium loadings for long term storage behavior studies. One sample has been used to collect pure tritium isotherm data on an annual basis. Last year when the annual isotherm was attempted, a leak occurred causing high hood activity. This required that the procedure be stopped until the leak

source could be detected and corrected. It was later determined that the valve located immediately above the sample cell had been the leak point.

On May 24, 1999 this valve was removed per procedure. This was accomplished by evacuating the sample and backfilling with argon. Then the cell and valve were separated from the rest of the mounting assembly, the valve was removed, and the Ti-3 sample was reattached to the assembly without using another valve. While this operation was designed to minimize exposure to air, the level of success achieved is unknown, and this represents another Ti-3 specific that is different from the other Ti samples.

Prior to this procedure a grab sample of the overpressure was taken, and it analyzed at 99.983% ^{3}He. The pressure obtained in the grab sampling apparatus back calculates to a pressure of 882 torr in the Ti-3 sample cell prior to sampling. (This point has been added to the plot of Ti-3 cell pressure and is shown in Figure 2.) This is unusually high for Ti and deserves some comment.

Ti-3 contains 1.6 grams of titanium, and is routinely loaded to a T/Ti ratio of 1.5 prior to storage. This means that approximately 0.033 moles of Ti is in the cell, and the T loading is with 0.050 moles. If that amount of material was decayed for 1 year, there would be 5.46% loss of T with a concomitant amount of ^{3}He formed. Initially almost all of this ^{3}He was being retained in the bulk Ti. However, after year two, some of this ^{3}He began to show up in the gas phase. So if we assume 3 years worth of decay, in 1 year increments starting at T/Ti=1.5, then we would have potentially accumulated about 0.0082 moles of ^{3}He. If all this were released to the gas phase in the Ti-3 cell, whose volume was 9.5 cc, a room temperature pressure of 16,000 torr would have developed. Thus an internal cell pressure of 900 torr represents a release of about 5-6% of the total ^{3}He ever generated in the Ti-3 material. This is a worst case analysis, since some limited He removal occurred through grab sampling and isotherm determinations. Typically, powdered hydrides will show 3-5% release of the total generated He, so the nominal behavior of Ti-3 is not out of line.

But as noted last year, the Ti-3 overpressure had begun to rise with time, and the increase now seems significant when compared to prior data (see Figure 2). (The aborted attempt to collect the FY98 isotherm data is not shown in the experimental work period bars of Figure 2.) The rate of pressure increase change noted in the HSV seems to validate the observed increasing amount of release observed in Ti-3. In Figure 3, the on-board pressure

sensor readings are shown for those Ti samples that have such a sensor attached. Clearly, Ti-3 is showing significantly different behavior, with a much increased slope of pressure increase when compared to the other samples. (Table 1 shows the critical parameters for the samples.)

Table 1. Titanium Tritide Samples' Pressure and Loading Data

Sample	g Ti	Pi(1)	Pf (2)	Vc	Q/Ti	%T
Ti-1	0.75	1.4	3.1	10.4	1.9	100
Ti-2	1.60	22.9	64.7	10.4	1.6	100
Ti-3	1.61	17.4	(3)	9.4	1.5	100
Ti-4	1.63	4.6	27.1	10.8	1.8	50
Ti-6	1.59	2.8	4.0	15.1	1.5	50
Ti-9	1.00	215.2	244.2	(4)	1.9+	100

(1) Earliest Recorded Pressure in torr
(2) Final Pressure in torr
(3) No recent sensor readings, 882 torr calculated
(4) Total cell volume unknown for replenished configuration

The only other Ti sample to show an unusual pressure increase is Ti-2. However, it was also used to determine some virgin material isotherms. Thus the similarity between Ti-2 and Ti-3 is the possibility of some physical change due to cycling. Typically this change is a decrepitation process. This would increase the surface to volume ratio and decrease the average particle size, both of which would facilitate ^{3}He release.

In the case of Ti-3, we could assume the several isotherms conducted over the years have pulverized the sample. This would explain the significantly greater rate of He release noted in Ti-3, since the Ti materials used in this study were large 'chunks' of material as opposed to a fine powder. This is however just an assumption until the sample is physically examined.

Ti-4 appears to show a slight pressure increase at first glance, but closer examination shows that the latest pressure readings have remained essentially unchanged but nonzero. This may be due to a pressure sensor zero drift early on. All samples except Ti-3 have remained undisturbed since loading, and thus no sensor calibration checks have been performed.

The annual 650 °C isotherm(s) of Ti-3 were attempted, but again the sample showed some unusual and unexpected behavior. During the initial cycles of the desorption isotherm determination procedure, the sample showed excessive pressure increases, especially after an overnight pause in the procedure. Because of this, at cycle 13 (about halfway through the isotherm) a grab sample of the gas over the sample was taken. It analyzed as 33.6% ^{3}He and 64.5% T (97.3% H isotopes purity). At the end of the isotherm (cycle 28) another grab sample was taken, and it analyzed as 19.2% ^{3}He and 76.8% T (95.4% purity). This excessive ^{3}He content combined with the apparent change in %^{3}He with cycle, made the extraction of the T isotherm from the data nearly impossible without severe assumptions about the amount of ^{3}He present at a given time.

During a subsequent isotherm, several samples were taken, and most translated to an approximately constant background of ^{3}He of 5-6 torr. This isotherm was much more behaved that the first one, but since no independent way of assessing the T/Ti ratio was used, the isotherm was tied to the prior one, which implies that we also could not correctly place it on the T/Ti scale. The shape of this isotherm was essentially the same as those obtained and reported in FY97.

The apparently rapidly varying ^{3}He release during the first isotherm followed by the almost constant release in the second is reminiscent of behavior of aged U beds we have also recently examined. In that case, we also observe an initially high ^{3}He release, followed by a tailing off to a constant but non-zero release rate. In both the U and Ti cases, the rate of ^{3}He release is clearly different from that of hydrogen release.

The utility of Ti-3 as an indicator of what might be happening in the HSV is at an end. Having removed much of the sample's ^{3}He, the state of the material does not mimic well that of the Ti in the HSV. Thus a new sample must supply the annual isotherms.

Pathforward

In FY00, the HSV will continue to be monitored and a new sample will have to be chosen for the annual isotherm.

There are some crucial questions to be answered,

- What caused Ti-3 to begin releasing ^{3}He?
- How much ^{3}He will Ti-3 release?
- Are other samples also releasing ^{3}He?

And most importantly,

- Will an HSV suffer release of ^{3}He when it is unloaded?

It may therefore be worthwhile to sample the overpressure (and measure the magnitude) on all 8 remaining Ti samples. Ti-3 can potentially be retired and physically examined, or it can be reloaded and aged further. Discussions will be held early in FY00 to decide what course of action is best. However, it is clear that more than the usual level of work needs to be invested at this time.

Figure 1. Uncorrected HSV-002 Overpressure

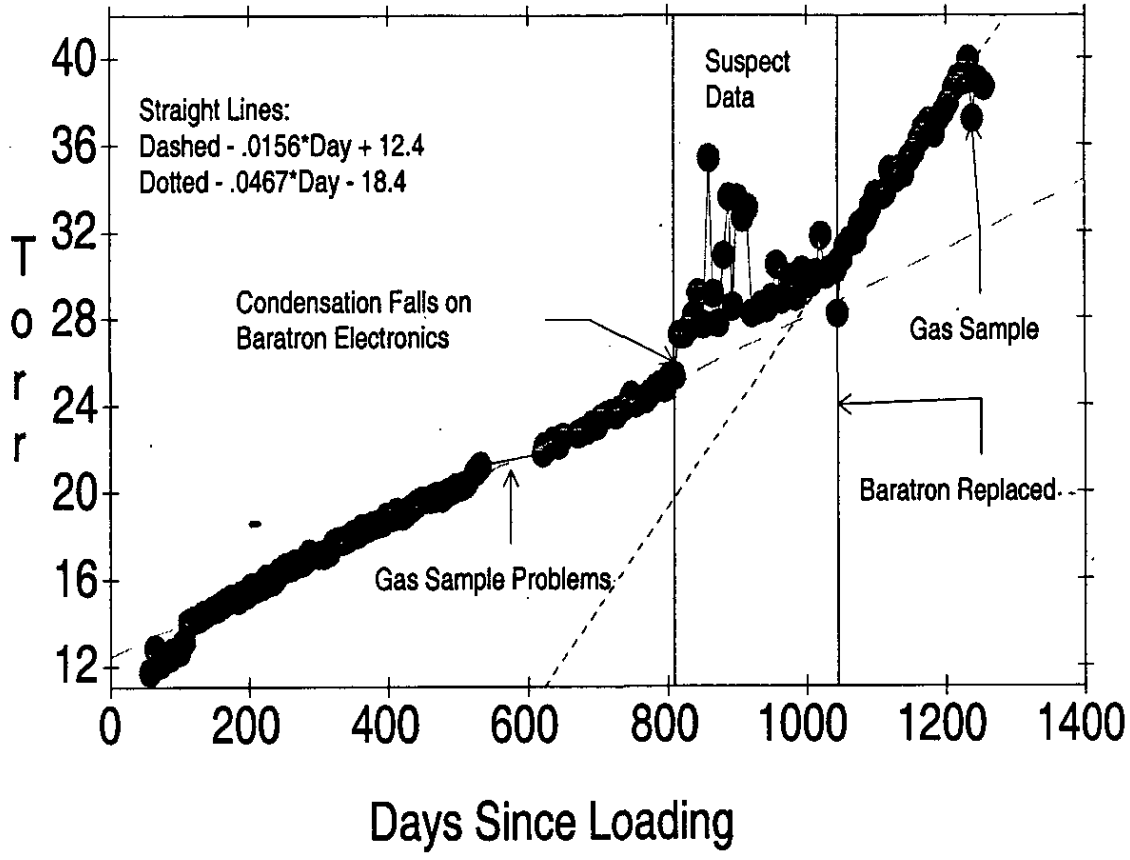


Figure 2. Ti-3 Cell Pressure with Time

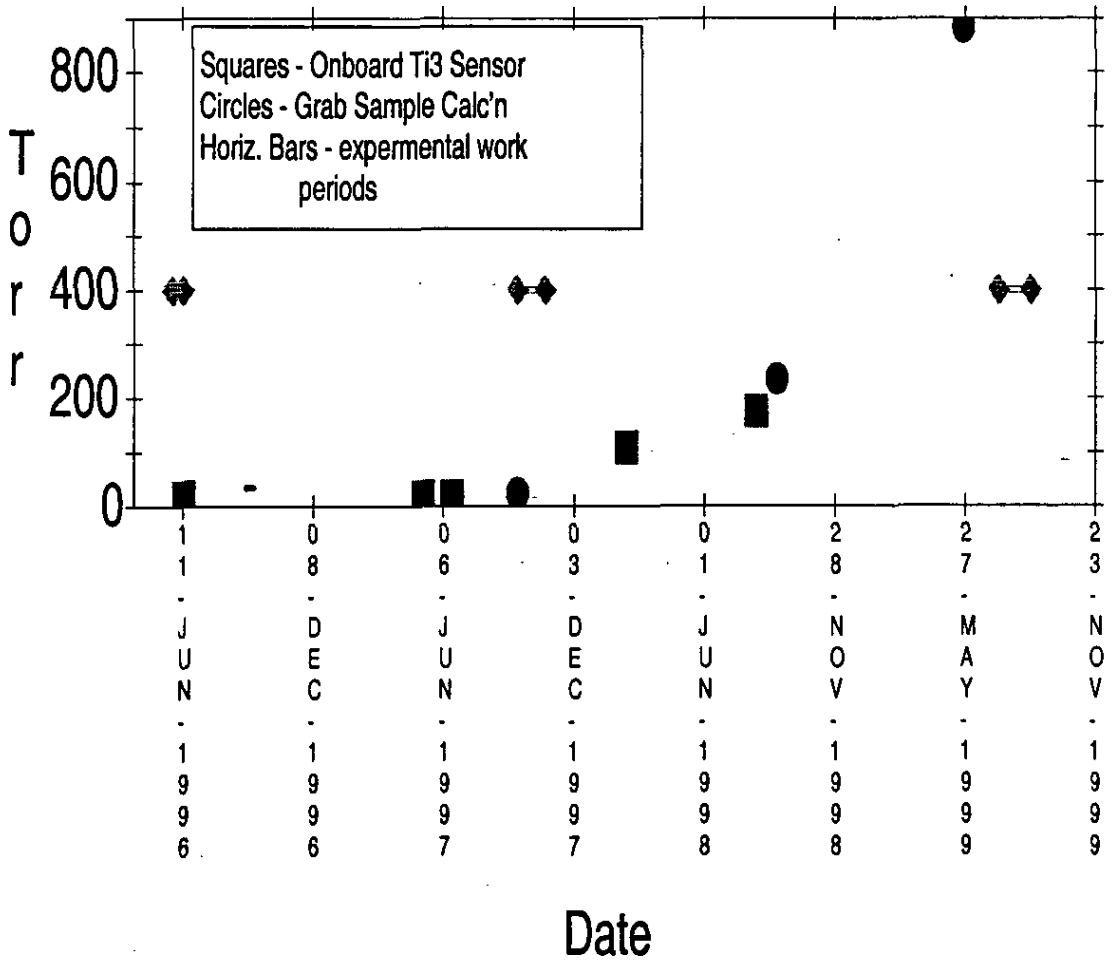
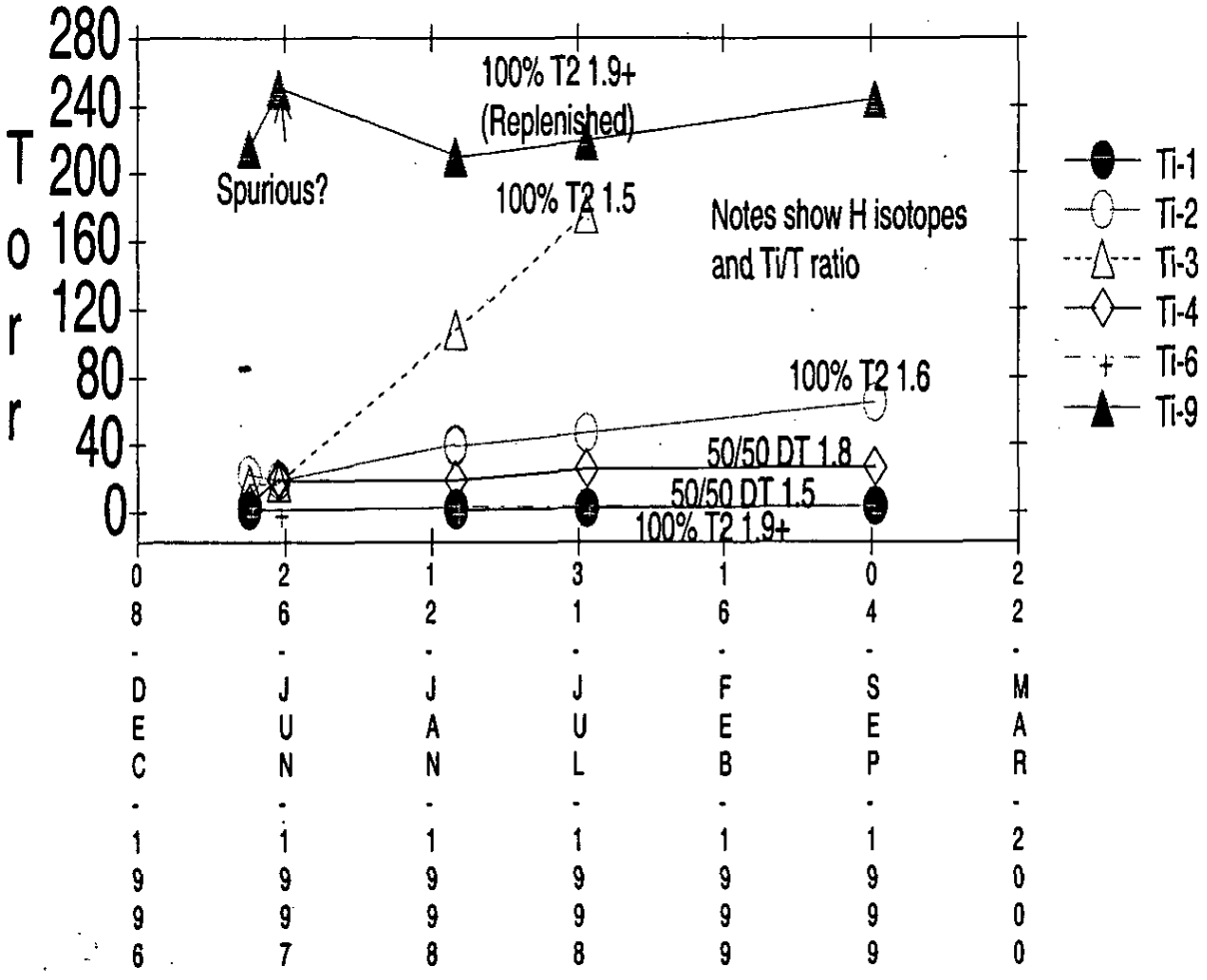


Fig. 3. On-Board Pressure Sensor Readings for Ti Samples



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Document Approval Sheet

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Title
FY99 Status Report on the HSV (U)

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Organization Code	Organization (No Abbreviations)
L2630	Savannah River Technology Center/Strategic Materials Technology Dept.

Other Authors: none

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October 4, 1999

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K. **DESCRIPTION/ABSTRACT**

The HSV in storage in MTF has been monitored during FY99, and its overpressure has been sampled and analyzed. The HSV's internal pressure continues to rise slowly, and the overpressure still analyzes as 100 percent ^{3}He. The titanium tritide sample that was to be monitored annually and which had developed a leak last year has been repaired and isotherms measured. Unfortunately the sample was showing significant unexpected 3He release, so the isotherm data is corrupted by unknown levels of 3He. This release has disqualified this sample for future use, as it is now seriously divergent from the HSV material. A different sample must be selected for subsequent studies.

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