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END-OF-LIFE SHUTDOWN STUDIES

INTERIM REPORT

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By

K. E. MOORE

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ABSTRACT

Dissociation pressure studies have been conducted to obtain a measure of the effect of tritium additions on the dissociation pressure of zirconium hydride. It was found that 1% tritium additions did not measurably affect the total pressure. Additional studies performed on ZrH_x and ZrT_y have shown that $ZrT_{1.70}$ has a dissociation pressure 1.6 times that of $ZrH_{1.70}$.

Annealing experiments were performed on U- ZrH_x fuel specimens containing measured amounts of tritium and helium-3. Density measurements on fuel specimens annealed at 1300 and 1500°F showed that the 3He resulting from 1% tritium additions will have a negligible effect compared to irradiation-induced fuel swelling and growth.

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I. INTRODUCTION

It has been shown⁽¹⁾ that in many aerospace reactor missions, a reliable shutdown device is required to reduce the potential radiological hazards presented by a nuclear reactor that returns from orbit. The decay of tritium ($T_{1/2} = 12.26$ yr) to the high absorption cross section helium-3 (5400 barns) provides an inherently reliable mechanism for shutdown. For orbit lifetimes greater than ~ 5 yr, the tritium-helium shutdown mechanism is practically as effective in reducing radiological hazards from reentering SNAP reactors as prompt shutdown at the end of a 1-yr mission. From preliminary design and development considerations, incorporating tritium as a tritide in the present SNAP reactor designs appears feasible without significantly affecting mission operation or power system reliability. Moreover, the reliability of the tritium-helium shutdown is considerably greater than that of mechanical (control rods or drums) or explosive devices.

The tritium loadings presently being considered for use in SNAP reactors are given in Table 1.

TABLE 1
TRITIUM LOADINGS UNDER CONSIDERATION
(Assuming Uniform Distribution in All Fuel Rods)

Reactor Type	Initial Tritium (10^{19} atoms/cc)	Helium-3 After 1 yr (10^{17} atoms/cc)	Reactivity Effect (\$)
SNAP 10A/2	0.56	3.1	-4
SNAP 8	0.53	2.9	-4
SNAP 8	1.6	8.7	-12

The purpose of the present work, which was conducted as a portion of the overall Aerospace Nuclear Safety Program, is to determine the feasibility of incorporating tritium into SNAP fuel. Specifically, the purpose of this work is to determine:

- 1) The effect of additions of tritium on the dissociation pressure of SNAP fuel
- 2) The amount of fuel swelling that occurs due to the presence of ^3He in the fuel

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Figure 1. Comparison of Dissociation Pressures of $\text{ZrD}_{1.50}$ and $\text{ZrH}_{1.53}$ (from data of Morton and Stark and of Edwards et al.)

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Figure 2. Dissociation Pressures for Hydrogen Isotopes (from data of Haag and Shipko)

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- 3) The permeation rates of hydrogen and tritium through a SNAP fuel-cladding assembly
- 4) The redistribution rate of tritium within SNAP fuel as a function of temperature
- 5) The rate of ^3He evolution from SNAP fuel as a function of temperature
- 6) A practical process to incorporate tritium into SNAP fuel elements, to test this process, and to write a process specification.

At the present time steps 1 and 2 have been completed and these results are given in this interim report.

A. DISSOCIATION PRESSURE MEASUREMENTS

The only known hydrogen isotope-zirconium dissociation pressure studies reported to date were performed by Morton and Stark.⁽²⁾ In this work they measured the dissociation pressures of zirconium deuteride (ZrD) as functions of composition ($\text{ZrD}_{0.02-1.80}$) and temperature. Plotted in Figure 1 are the $\text{ZrD}_{1.50}$ isochore extracted from the isotherm data reported in their work and the $\text{ZrH}_{1.53}$ isochore, extrapolated from the low millimeter pressure range and reported by Edwards, Levesque, and Cubicciotti.⁽³⁾

These data indicate that $\text{ZrD}_{1.50}$ has about an order of magnitude greater dissociation pressure than $\text{ZrH}_{1.50}$. However, work reported by Haag and Shipko⁽⁴⁾ on titanium hydride, deuteride, and tritide indicated that there was essentially no difference in the dissociation pressures of these compounds. A portion of their work illustrating these data is shown in Figure 2.

Lacking literature data on the zirconium tritide system, and since it was not possible to predict the effect of tritium on the dissociation pressure of the fuel, it was necessary to measure it experimentally.

B. ANNEALING EXPERIMENTS

Annealing experiments performed on metals containing inert gases formed by irradiation^(5, 6) or cyclotron injection have proved useful for measuring inert gas-induced swelling.⁽⁷⁾ Inert gas-induced swelling measurements were made by obtaining densities before and after annealing the inert gas-bearing metal, at elevated temperatures. Similar techniques were employed herein to measure the extent of ^3He -induced SNAP fuel swelling.

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a. Equipment

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b. Schematic

Figure 3. Modified Sieverts' Apparatus

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II. EQUIPMENT AND MATERIALS

A. DISSOCIATION PRESSURE APPARATUS

Shown in Figure 3 is the modified Sieverts' apparatus used for measuring dissociation pressures.

Teflon O-ring stopcocks were used throughout the glass portions of the system instead of ground glass stopcocks to avoid the use of stopcock greases that would enhance the degradation of tritium by exchange with hydrogen.

Zirconium metal samples weighing about 8 g were cleaned in a solution consisting of water, nitric acid, and hydrofluoric acid in the volume ratios of 50, 45, and 5, respectively. They were then rinsed in ethyl alcohol, dried, and weighed. The cleaned zirconium samples were placed in a molybdenum crucible and this secondary container was then inserted into a quartz retort. The retort was heated and maintained at the desired temperature to within $\pm 0.5^\circ\text{C}$ with a Marshall resistance furnace and saturable core reactor coupled with a Wheelco controller. To assure a uniform temperature profile in the furnace, a massive stainless steel heat sink was used. Temperatures were measured with a Leeds and Northrup potentiometer and a Chromel-Alumel thermocouple.

Two flasks, CV_1 -500 cc and CV_2 -2000 cc, were calibrated with water to ± 0.02 cc and ± 0.5 cc, respectively. These calibrated volumes were in turn used to calibrate the various portions of the system manifold with hydrogen gas. A cathetometer was used to measure pressures on a 0- to 800-mm mercury manometer to ± 0.1 mm.

Since an undefined temperature gradient (from ambient to the specimen temperature) was present along the specimen retort, it was necessary to calibrate the "effective volume" of the retort as a function of temperature. This was done in the following manner: (1) hydrogen gas was admitted into the volume of the system manifold between valves 1 and 3 and the mercury column, V_1 ; (2) the pressure, P_1 , and the ambient temperature, T_1 , were recorded; (3) this quantity of gas was then expanded from V_1 into V_2 (V_1 plus V_R , the retort volume); (4) the new pressure, P_2 , any change in ambient temperature, T_2 , and the retort temperature were recorded; (5) the volume occupied by V_2 was calculated as though the entire volume were at ambient temperature, where:

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$$V_2 = P_1 V_1 T_2 / P_2 T_1$$

$$V_R, \text{ at any retort temperature} = V_2 - V_1$$

Using this technique, a plot of V_R vs retort temperature from ambient to 800°C was established.

The necessary corrections were made to account for the change in V_1 governed by the height and diameter of the mercury column.

Tritium gas, supplied by Oak Ridge National Laboratories, was stored in the form of UT_3 in a uranium bed enclosed in Type 304 stainless steel. The inner and outer surfaces were coated with Solaramic* glass to minimize the diffusion of tritium through the container walls upon subsequent heating of the bed. A fritted glass filter was inserted between the uranium bed and the system manifold to prevent uranium powder from getting into the manifold.

The uranium bed was recharged with 500 to 600 cc of tritium several times during these experiments. Periodic mass spectrometric analyses indicated that the isotopic content of the tritium was always greater than 95%. Tritium gas was expanded into the system manifold at the desired pressure by controlling the temperature of the bed. Residual gas remaining in the lines could conveniently be reabsorbed on the bed. 3He was stripped off the bed prior to an experimental run via the vacuum pumps.

The "ultra pure" hydrogen gas used in these tests had a total impurity content of less than 10 ppm.

Hafnium-free crystal bar zirconium metal used in these tests was analyzed for its impurity content. Table 2 contains the results of this analysis.

B. ANNEALING EXPERIMENTS

The dissociation pressure measuring apparatus was used to tritide and hydride 90 wt % zirconium—10 wt % natural uranium, 0.15 wt % carbon-modified specimens.

The samples were encapsulated under a 10^{-3} -mm Hg vacuum in heavy-wall (2-mm) quartz 10-mm ID tubing prior to annealing in Marshall resistance furnaces. At annealing temperatures higher than 1350°F, tungsten foil was inserted into the quartz tubing to prevent a contact reaction between SiO_2 and the zirconium in the specimens.

*A proprietary composition marketed by Solar Division, International Harvester Corp., San Diego, California

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TABLE 2
TYPICAL CHEMICAL ANALYSIS OF ZIRCONIUM METAL

Element	ppm	Element	ppm
Hf	<100	Fe	300
O	65	Li	2
C	100	Mg	10
N	25	Mn	5
H	14	Mo	10
Al	150	Na	50
B	3	Ni	10
Ba	<10	Pb	20
Be	20	Si	250
Bi	<5	Sn	10
Ca	<20	Ti	100
Cd	0.5	V	30
Co	<2	Zn	25
Cr	<400		

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III. EXPERIMENTAL PROCEDURE

A. DISSOCIATION PRESSURE MEASUREMENTS

Comparisons of the dissociation pressures of ZrH_x and $ZrH_{(x-y)}T_y$ were made by first measuring the dissociation pressures of a ZrH_x sample over a range of temperatures and pressures. Next, a measured portion of hydrogen was removed from the sample and replaced with an equal portion of tritium. The dissociation pressures of the new sample, $ZrH_{x-y}T_y$, were measured over the same range of temperatures. Direct comparisons could then be made of the pressure vs temperature curves of the data.

The composition of the sample varied during an experimental run as a function of the internal volume of the system manifold and the temperature, dissociation pressure, and mass of the sample. Since all of these are measurable quantities, it was possible to determine the H/Zr ratio of the specimen at any temperature.

Prior to hydriding, the zirconium metal was outgassed at 850°C for 20 hr under high vacuum. Hydriding was accomplished by admitting an accurately measured quantity of hydrogen into the retort containing the sample at about 650°C. When the desired composition was obtained, valve 3 (refer to Figure 3b) was closed and the dissociation pressure measurements were begun. The sample was held at temperature for 1.5 to 24 hr before recording the dissociation pressure. Subsequent to obtaining dissociation pressures at temperatures ranging from 550 to 800°C, a measured quantity of hydrogen was removed from the sample and was replaced with an equal quantity of tritium. (The isotopic purity of tritium was measured by mass spectrometry prior to tritiding.) The $ZrH_{(x-y)}T_y$ sample was allowed to equilibrate for 24 hr at 550°C, at which time the dissociation pressures were again measured over the same range of temperatures.

A similar procedure was used in tests in which ZrH_x and ZrT_y dissociation pressures were measured. The tritium used had an isotopic purity of greater than 97% as measured by mass spectrometry before and after the ZrT_y experimental runs.

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B. ANNEALING EXPERIMENTS

The apparatus shown in Figure 3 was used for preparation of fuel swelling samples. Fuel specimens nominally 0.3 in. in diameter by 0.4 in. long were tritided with tritium of known purity at 850°C to the desired composition ($T/Zr \leq 0.20$). By tritiding before adding hydrogen, the activity of the gas in the system manifold could be quickly reduced to a reasonably safe level, since the tritiding reaction proceeded rapidly in the low-"hydrogen"-composition β phase. Hydriding proceeded from this point to the desired over-all H/Zr ratio. This normally took about 5 to 6 hr. Hydriding across the $\beta + \delta$ field proceeded very slowly, and any attempt to accelerate the hydriding rate in this region resulted in cracked specimens.

The quantity of tritium absorbed by the sample during the initial tritiding step was calculated from pressure-volume relationships. The actual quantity remaining in the sample at the conclusion of the hydriding step was established by measuring the T/H ratio of the gas remaining in the system manifold and using P-V relationships. This value was verified by weight gain and material balance considerations.

Knowing the initial quantity and activity of tritium, the ^3He formed within the fuel at any point in time could be calculated.

Density measurements, using water as a fluid medium, were made on the $\text{U-ZrH}_x\text{T}_y$ fuel specimens. They were then vacuum-encapsulated in quartz at a pressure of 10^{-3} mm Hg and annealed at either 1300°F for 840 to 930 hr, or 1500°F for 21 to 262 hr. Density measurements made on annealed specimens were compared with preannealing densities to establish whether volumetric changes resulting from the presence of ^3He had occurred. When annealed at elevated temperatures, ^3He present in the metal hydride matrix could possibly migrate, collect as small gas pockets, and exert a significant gas pressure on the surrounding matrix. If this pressure should exceed the strength of the matrix material, deformation of the fuel body would occur.

At temperature, the quantity of T and H in equilibrium with the sample did not significantly change the composition of the sample, since the void volume of the quartz capsules was only 8 to 10 cc.

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TABLE 4
COMPARATIVE DISSOCIATION
PRESSURE DATA FOR
 $ZrH_{1.64-1.83}$ AND
 $ZrH_{1.62-1.81}T_{0.017}$

Temperature (°C)	Pressure (mm Hg)	$\frac{H}{Zr}$	$\frac{H+T}{Zr}$
543	25.8	1.829	-
559	37.0	-	1.826
596	83.0	-	1.815
598	91.5	1.809	-
641	192.7	1.777	-
649	208.8	-	1.772
687	305.0	1.741	-
706	350.0	-	1.727
727	427.0	1.702	-
744	454.8	-	1.692
792	621.0	1.638	-
796	622.2	-	1.638

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Figure 5. Dissociation Pressure vs
Temperature Curves for
 $ZrH_{1.64-1.83}$ and $ZrH_{1.62-1.81}T_{0.017}$

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Figure 6. Dissociation Pressure vs
Temperature Curves for
 $ZrH_{1.64-1.83}$ and $ZrH_{1.62-1.81}T_{0.023}$

TABLE 5
COMPARATIVE DISSOCIATION
PRESSURE DATA FOR
 $ZrH_{1.64-1.83}$ AND
 $ZrH_{1.62-1.81}T_{0.023}$

Temperature (°C)	Pressure (mm Hg)	$\frac{H}{Zr}$	$\frac{H+T}{Zr}$
557	38.5	-	1.827
567	48.4	1.824	-
585	90.9	-	1.811
608	112.5	1.804	-
628	159.0	-	1.790
670	275.0	1.753	-
680	301.0	-	1.745
711	384.7	1.718	-
720	412.0	-	1.710
751	502.8	1.679	-
755	518.2	-	1.675
785	610.7	-	1.643
791	630.7	1.636	-

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TABLE 6
COMPARATIVE DISSOCIATION
PRESSURE DATA FOR
ZrH_{1.66-1.80} AND
ZrH_{1.62-1.81}T_{0.017}

Temperature (°C)	Pressure (mm Hg)	$\frac{H}{Zr}$	$\frac{H+T}{Zr}$
577	42.2	-	1.805
596	56.6	1.803	-
620	106.1	-	1.788
643	144.5	1.779	-
682	265.4	-	1.742
684	269.0	1.742	-
691	288.8	1.739	-
714	358.7	-	1.716
768	534.8	-	1.666
776	547.2	1.666	-

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Figure 7. Dissociation Pressure vs
Temperature Curves for
ZrH_{1.66-1.80} and
ZrH_{1.57-1.71}T_{0.09}

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Figure 8. Results of 1300 and 1500°F
Anneal of Fuel Swelling Samples

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TABLE 7
RESULTS OF 1300°F ANNEAL OF FUEL-SWELLING SAMPLES

Sample	$\frac{H+T}{Zr}$	Final ^3He Concentration (10^{19} atoms/cc)	Time at Temperature (hr)	Change in Density (± 0.006 g/cc)
W-1	1.70	1.0	840	+0.006
W-2	1.70	1.0	840	+0.002
W-3	1.70	1.0	840	-0.001
W-4	1.70	3.5	930	+0.004
W-5	1.70	3.5	930	-0.009

TABLE 8
RESULTS OF 1500°F ANNEAL OF FUEL-SWELLING SAMPLES

Sample	$\frac{H+T}{Zr}$	Final ^3He Concentration (10^{19} atoms/cc)	Total Time at Temperature (hr)	Cumulative Change in Density (± 0.006 g/cc)
W-1*	1.68	1.0	21	+0.006
W-2*	1.68	1.0	21	0.000
W-4*	1.68	3.5	21	-0.010
W-4*	1.68	3.5	87	-0.009
W-5*	1.68	3.5	21	-0.006
W-9	1.63	1.6	42	-0.005
W-9	1.63	1.6	91	+0.002
W-10	1.63	1.6	42	-0.007
W-10	1.63	1.6	91	0.000
W-11	1.63	1.6	42	-0.002
W-17	1.63	3.5	262	+0.012
W-18	1.63	3.5	262	-0.003
W-19	1.63	3.5	24	-0.010
W-20	1.63	3.5	24	-0.013
W-21	1.63	4.5	24	-0.013
W-23	1.63	3.5	24	-0.010
W-24	1.63	3.5	24	-0.012
W-25	1.63	3.5	24	-0.010
W-26	1.63	3.5	24	-0.009

*Preannealed at 1300°F for 840 to 930 hr

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V. DISCUSSION

A. DISSOCIATION PRESSURE MEASUREMENTS

The dissociation pressures obtained in this work for ZrH_x ($x = 1.65$ to 1.85) are approximately 20% lower than those obtained by Raymond⁽⁸⁾ over the same range of hydrogen compositions, temperatures, and pressures. This apparent discrepancy is probably the result of the much lower interstitial impurity (oxygen, nitrogen, and carbon) content of the material used in this work (see Table 2 for chemical analyses of the zirconium metal). But since the primary purpose of this work was to measure the effect of tritium additions on the dissociation pressure of zirconium hydride, it is of minor importance to establish the degree of agreement of these data with data of other investigators.

Isochores for $\text{ZrH}_{1.70}$ and $\text{ZrT}_{1.70}$ were plotted in Figure 4 in addition to the curves obtained from four dissociation pressure runs. These isochore curves are parallel, and $\text{ZrT}_{1.70}$ has a dissociation pressure 1.6 times that of $\text{ZrH}_{1.70}$ within the range of temperatures and pressures investigated.

Figures 5, 6, and 7 contain curves obtained for comparisons between ZrH_x ($x = 1.65$ to 1.85) and $\text{ZrH}_{(x-y)}\text{T}_y$ where $y = 0.017$, 0.023 , and 0.09 , respectively, at room temperature. All of the data points obtained for $y = 0.017$ and 0.023 fell on the ZrH_x curves, indicating that no measurable pressure difference exists at these tritium concentrations. These tritium concentrations are at least 10 times the concentrations being considered for use (see Table 1).

As depicted by the dotted curve in Figure 7, $\text{ZrH}_{(x-y)}\text{T}_y$ ($y = 0.09$) had a slightly higher dissociation pressure over a portion of the curve, while the remainder of the points fell on the ZrH_x curve.

B. ANNEALING EXPERIMENTS

The ^3He concentrations contained in these specimens are considerably higher than could be formed from proposed tritium loadings given in Table 1. As can be seen from Table 8, the largest density change, $\Delta\rho = 0.013$ g/cc, occurred at 1500°F in a sample which contained 4.5×10^{19} atoms/cc of ^3He (after "cooling" at room temperature for 45 days). This $\Delta\rho$ corresponds to an increase in volume of 0.21%. This amount of swelling is insignificant in terms of the swelling that occurs in SNAP fuel after 12,000 hr of reactor operation.

As pointed out in Section IV-B concerning the results of annealing experiments, the 1500°F isotherm data points represented in Figure 8 are the average values obtained after annealing the samples 21 to 41 hr. Upon further annealing at 1500°F for 87 to 91 hr, the densities of the samples increased. Based on weight loss measurements, the samples lost about 1.5% of their hydrogen. This quantity of hydrogen would account for a density increase of 0.004 g/cc,⁽⁹⁾ which appears to be consistent with the $+\Delta\rho$ resulting from the additional annealing time. For this reason it seems apparent that a major portion of the ^3He -induced swelling occurred within 21 to 41 hr. The samples annealed at 1300°F for up to 930 hr lost about 1% of their hydrogen, which corresponds to a $+\Delta\rho$ of about 0.002 g/cc. Since the weight loss can only be used as approximation of the hydrogen (and tritium) loss, no attempt was made to correct the density values for hydrogen loss.

Four samples, two at an H/Zr ratio = 1.63 and two at an H/Zr ratio = 1.37 (W-12, 13 and W-15, 16) each at a ^3He concentration of 3.5×10^{19} atoms/cc, were annealed at 1500°F for 24 hr. All of these samples contained macrocracks after the annealing cycle. Typical cross sections of these samples are shown in Figure 9.

a. Sample 13

b. Sample 15

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Figure 9. Photomicrographs of Samples 13 and 15
After a 1500°F Annealing Cycle

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In an effort to duplicate this occurrence, seven additional samples (W-19 through -21 and W-23 through -26) were prepared and annealed in the same manner. These samples, all with an H/Zr of 1.63, were found to be free of surface cracks upon postanneal examination. Samples W-19 and -20 were then cooled at room temperature until a ^3He concentration of approximately 1×10^{20} atoms/cc were formed in them. At this time these samples were reannealed at 1500°F for about 24 hr. They were also free of surface cracks.

To further investigate cracking of those samples, samples W-3, -4, -5, and -11 were prepared metallographically and examined at 1000X after their respective annealing cycles. These samples were found to be free of micro-cracks or voids.

It was first reasoned that ^3He bubble formation initiated cracking in samples W-12, 13 and 15, 16. However, no further evidence has been found to support this theory. Based on the postanneal condition of the remainder of the samples annealed at 1500°F , it seems more likely that the cracking occurred as the result of some anomaly occurring during hydriding of these samples rather than the direct result of ^3He formation.

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VI. DISCUSSION OF ERRORS

A. DISSOCIATION PRESSURE MEASUREMENTS

Pressures were read on the manometer to a precision of ± 0.1 mm Hg but were probably accurate to ± 0.5 mm Hg. The largest single factor influencing the accuracy of the dissociation pressure measurements was the control of temperature. Pressure changes due to fluctuations in temperature, after establishing equilibrium, were of the order of ± 1 mm Hg.

The ambient temperature of the system manifold was measured with a strategically located Hg thermometer to $\pm 0.5^\circ\text{C}$. A 1°C variation in the temperature of the manifold could result in a 0.15% error in calculating the H/Zr ratio of the specimen.

B. ANNEALING EXPERIMENTS

A statistical analysis was performed on both the density data and the means by which the density measurements were made. It was found that density measurements were accurate to ± 0.006 g/cc at a 95% confidence level based on single measurements.

^3He concentrations, tabulated in Tables 7 and 8, were calculated from the activity and initial concentration of tritium. ^3He gas loss was ignored since the amount of ^3He that would be released at elevated temperatures has not been measured. However, measurements of ^3He release will be conducted in subsequent experiments for this program. It is not expected to be significant, as less than 0.2% of the fission gases are released from SNAP fuel during irradiation.

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VII. CONCLUSIONS

From these end-of-life shutdown studies the following conclusions were reached:

1) Tritium additions corresponding to as much as 1% of the (H+T)/Zr ratio do not measurably affect the dissociation pressure of SNAP fuel.

2) In the absence of reactor radiation, no significant fuel swelling is produced by ^3He concentrations as high as 4.5×10^{19} atoms/cc; this concentration is approximately 100 times that which would be produced in 1 yr by decay of tritium at the proposed loading concentrations.

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