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Hydrogen and Helium Gas Formation and their Release Kinetics in Tungsten Rods after Irradiation with 800 MeV Protons

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Abstract: In the Accelerator Production of Tritium Program, thermalized neutrons produced from multiplication and moderation of spallation neutrons will be absorbed in ^{3}He gas to produce tritium. The spallation neutrons will be generated by the interaction of high energy (1 GeV) protons with solid tungsten rods. An unavoidable byproduct of the spallation reactions will be large amounts of helium and hydrogen gas generated in the rods. The release kinetics of these gases during various proposed off-normal scenarios involving loss of coolant and after-heat induced rises in temperature is of particular interest. In addition, the magnitude of the gas generation cross sections and the fractional retention of these gases is necessary for extrapolation to higher exposures.

Tungsten rod specimens irradiated with 800 MeV protons in the Los Alamos Neutron Science Center to rather high exposures have been sectioned to produce small specimens suitable for measurement of both helium and hydrogen. Hydrogen evolution was measured both by dropping the specimen into a small ceramic crucible at 1200°C and also by subjecting the specimen to a simulated temperature ramp from ~200 to 1200°C. The latter technique showed four distinct hydrogen release peaks at temperatures of approximately 500, 800, 1000 and 1200°C, indicating a variety of trapping sites with different binding energies. Helium release and total content were measured by subjecting the specimens to a similar temperature excursion, followed later by melting to release the remaining helium. Approximately 99% of the helium was retained until melting occurred. For both gases, release measurements were conducted using mass spectrometric techniques.

The measured amounts of helium agreed well with predictions. The hydrogen measurements were lower than predicted. This may reflect diffusional losses from the rods or some problem with the evaporation model in the LAHET code.

Keywords: helium measurements, hydrogen measurements, Accelerator Production of Tritium (APT), hydrogen release, helium release, tungsten targets

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DISCLAIMER

Introduction

The Accelerator Production of Tritium (APT) project *[1]* was proposed as a solution to the national need for tritium. In the APT concept, high-energy protons would impinge on a tungsten target producing high-energy spallation neutrons. These neutrons would in turn be multiplied using a lead blanket, then thermalized using water. Tritium production would occur through capture of the thermalized neutrons by ^{3}He gas. A main technical issue that was addressed during the APT design was radiation damage to materials in the mixed high-energy proton and neutron environment. A materials irradiation program *[2]* using the 800-MeV proton accelerator at the Los Alamos Neutron Science Center (LANSCE) developed. To simulate the tungsten neutron source in the proposed APT target, a series of tungsten rods was included in the LANSCE materials irradiation assembly.

While reviewing postulated off normal conditions for the APT target, the question of gas buildup inside the Alloy 718 clad tungsten rods was raised. Spallation reactions typically result in large amounts of helium and hydrogen being produced in the target material. If enough gas is produced and released from the target material, and then trapped at the tungsten/cladding interface, this gas could result in the failure of the target cladding due to a pressure build-up. Therefore, the tungsten rods in the LANSCE materials irradiation were used to address two important questions; (1) is the produced gas released from the target material and at what rate, and (2) how accurately can gas production be predicted for the APT target?

Tungsten Analysis Samples

Several sets of tungsten samples were prepared at Los Alamos National Laboratory (LANL) for helium and hydrogen measurements. Each sample was in the form of a thin disk cut from selected 3.18 mm diameter tungsten target rods that had been irradiated with 800 MeV protons as part of the materials testing program. As the rods were highly radioactive, sample preparation was done in a hot cell. Extensive radiometric analysis was conducted on the samples to provide flux and gradient data for the model calculations. A diagram of the experimental setup in the LANCE facility is shown in Figure 1. Locations of the individual tungsten specimens, relative to the proton beam, are shown in Figure 2.

Samples for gas analysis were cut using small diagonal wire cutters. Prior to analysis, each specimen is individually cleaned in acetone and air-dried. The mass of each analyzed specimen was determined using a microbalance with calibration traceable to the National Institute of Standards and Technology (NIST). Mass uncertainty is conservatively estimated to be ±0.002 mg.

Helium Measurements

Helium Analysis System

Helium analyses were conducted by mass spectrometry at Pacific Northwest National Laboratory (PNNL). Details on the mass spectrometry system have been presented elsewhere *[3,4]*. Helium contents were determined by heating and/or vaporizing each sample in a resistance-heated crucible in one of the mass spectrometer system's high-temperature vacuum furnaces. Helium values were determined either by

direct measurements of the mass spectrometer helium signal, or by an isotope-dilution technique where the released helium is compared with a known quantity of added ^{3}He "spike". The helium spikes were obtained by expanding and partitioning known quantities of gas through a succession of calibrated volumes*[3]*. The mass spectrometer was calibrated for mass sensitivity during each series of runs by analyzing known mixtures of ^{3}He and ^{4}He. Reproducibility of the analysis system for samples with known homogeneous helium content is ~0.5%. Absolute accuracy is generally better than 1%.

Stepped-Anneal and Total Helium Measurements

Details of the stepped-anneal and total helium measurements have been presented earlier*[5]*. For the stepped-anneal helium release measurements, the specimens cut from the tungsten disks were loaded into the central section of a 0.48 cm diameter graphite crucible. Small graphite plugs were placed at each end of the hole to position the samples as close as possible to the middle of the crucible. Temperature measurements were conducted using either a thermocouple or an optical pyrometer. Temperature uncertainty is estimated to be ±50°C. As both ^{3}He and ^{4}He were expected in the samples, no ^{3}He spike was used.

Results of the stepped-anneal measurements conducted earlier are shown graphically in Figures 3 and 4. Helium results are plotted in atomic parts per million (appm), based on a calculated value of 0.328×10^{22} atoms per gram for tungsten. Helium levels were corrected for background helium buildup in the analysis furnace as a function of time, obtained from separate "control" analyses conducted immediately after the sample runs. For sample W-2, helium release is first observed at a temperature of ~800°C. From 800°C up to the final temperature of ~1600°C, the incremental helium release is approximately the same for each temperature step, although there is some indication of a slowly increasing release rate up to ~1400°C. At the final temperature of 1600°C, a total of five measurements were made, and these data show a leveling off of the gas release at a value of ~1.4 appm. Similar trends were observed for sample W-3, with the ^{4}He release tending asymptotically to ~1.0 appm at the highest temperature of ~1200°C. For this second sample, however, there is little evidence for an increasing helium release rate with temperature (above ~800°C). The ^{3}He release for both specimens was at or below the detection limit of the analysis system (~10^{12} atoms) for the particular setup used in these tests. Variability in the helium release curves is due largely to variability in the subtracted helium background*[5]*.

Following the stepped-anneal measurements, the two tungsten specimens were relocated, in their original crucibles, to different positions in the same furnace for subsequent vaporization analysis. For these measurements, the residual helium contained in the specimens was determined using the isotope-dilution method. Prior to the addition of the spike, however, a first aliquot of the sample gas was taken for a determination of the helium isotopic ratio in the sample itself.

Helium measurements in the two samples after vaporization are summarized in Table 1. Total helium measured was 753 appm for W-2 and 713 appm for W-3, with an average of 733 ± 28 (1σ) appm. The ^{4}He/^{3}He isotopic ratio observed in the two specimens was 13.9 and 13.7, respectively, with an average value of 13.8 ± 0.1 (1σ). The absolute uncertainty (1σ) in the helium contents is estimated to be between 1% and 2%.

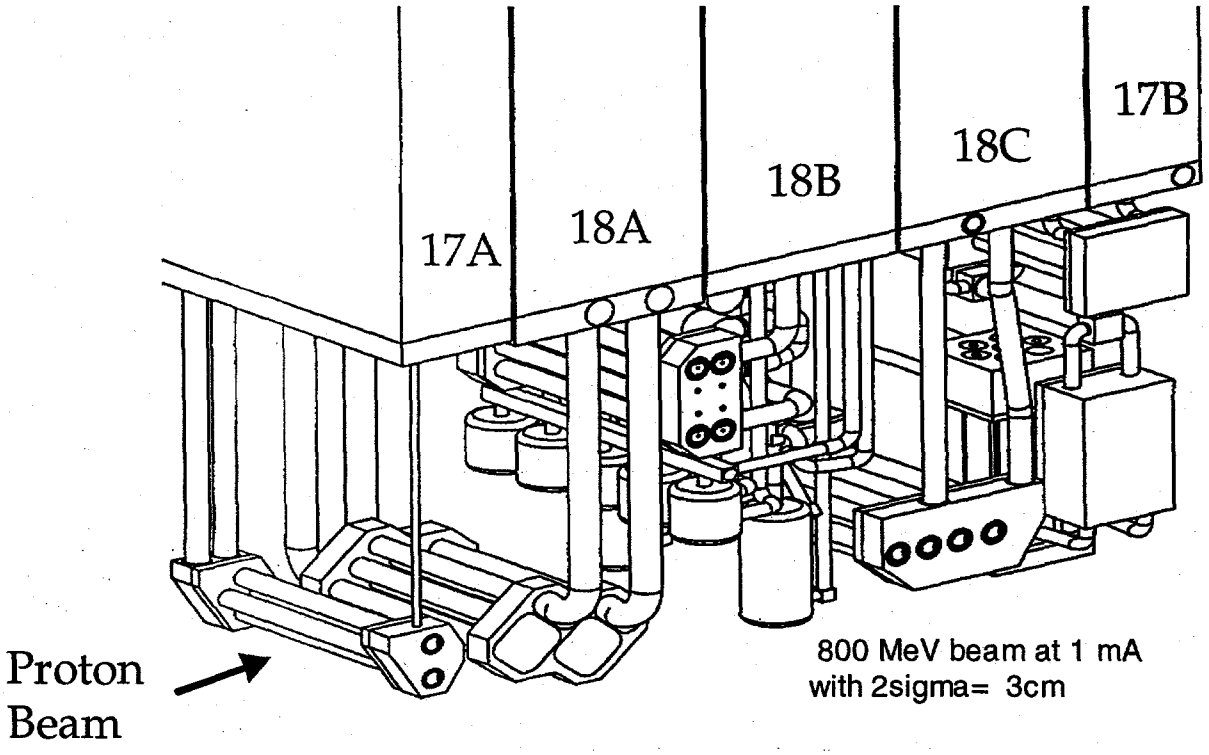

Figure 1 - *LANSCE A-6 Irradiation Setup*

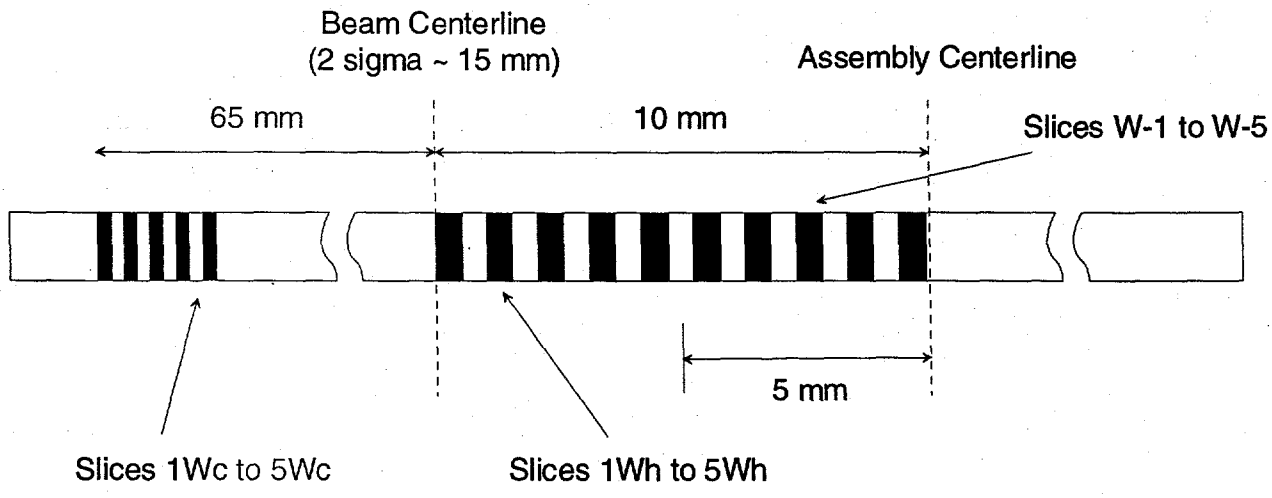

Figure 2 – Tungsten Sample Location Relative to Proton Beam

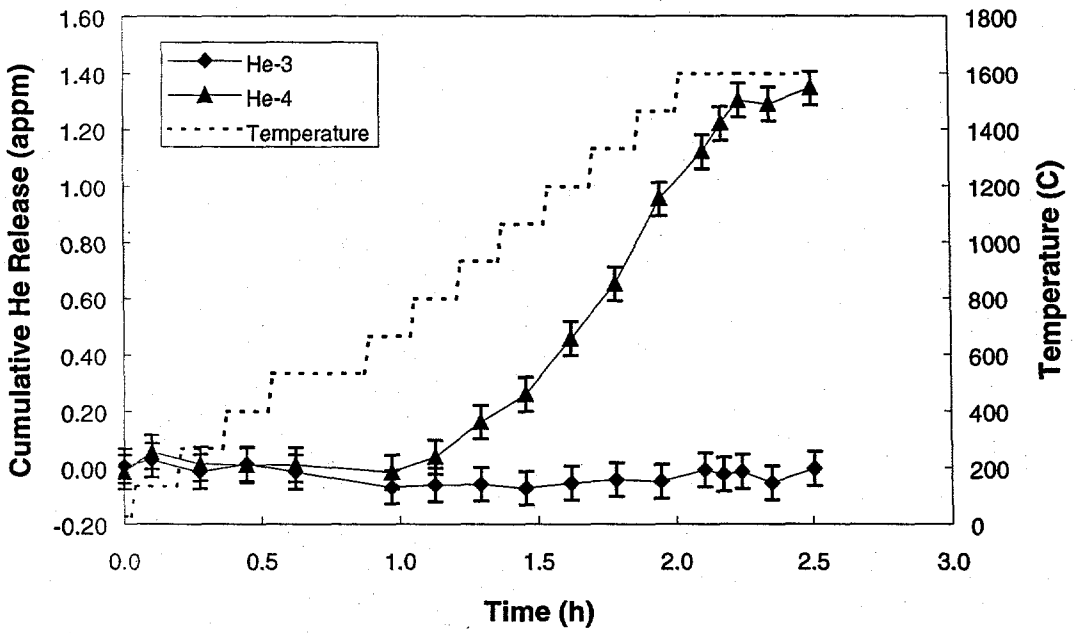

Figure 3 - *Helium Release in Sample W-2*

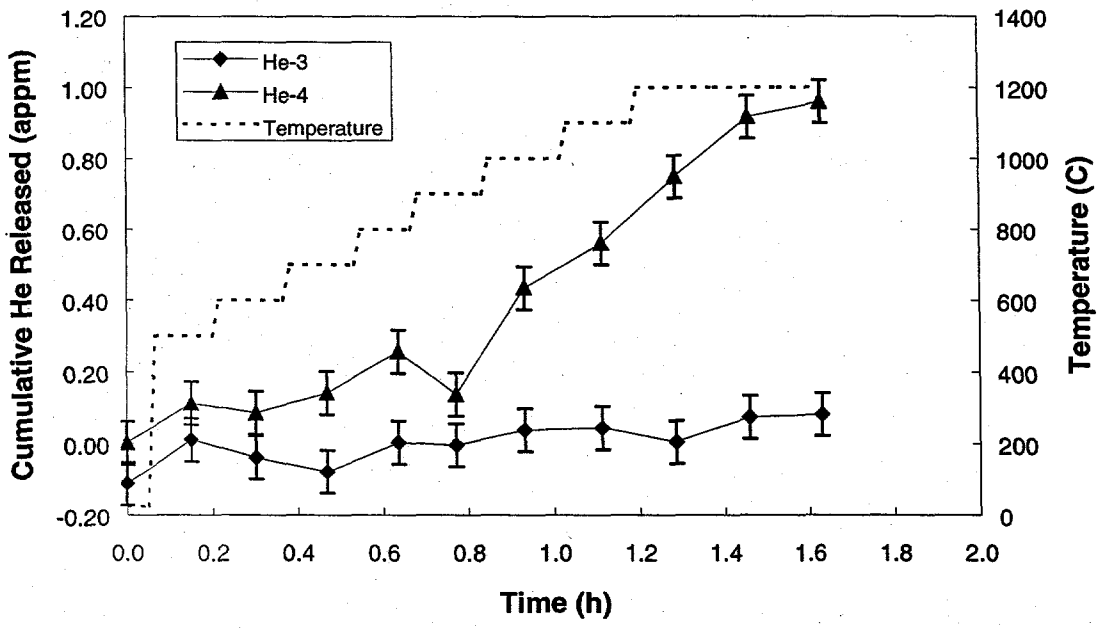

Figure 4 - *Helium Release in Sample W-3*

Table 1 – *Total Helium in APT Tungsten*

Specimen	Material	Analysis Type[a]	Specimen Mass[b] (mg)	Measured Helium (10^{13} atoms) ^{3}He	Measured Helium (10^{13} atoms) ^{4}He	Total Helium Concentration (appm)[c] ^{3}He	Total Helium Concentration (appm)[c] ^{4}He
W-2-B	Tungsten	Anneal	5.373	0.1	0.2		
		Vap.		8.9	123.4	51.0	703.4
W-3-B	Tungsten	Anneal	3.606	0.34	0.17		
		Vap.		5.74	78.50	48.9	665.9
1Wc-E		Vap.	3.510	0.268	2.570	2.33	22.35
-F		Vap	5.965	0.460	4.043	2.35	20.69

[a]Stepped-anneal or vaporization analysis.
[b]Mass uncertainty is ±0.002 mg.
[c]Total helium concentration in atomic parts per million (10^{-6} atom fraction) with respect to the total number of atoms in the specimen. Values for the W-2 and W-3 represent the total of the stepped-anneal and vaporization analyses.
[d]Mean and standard deviation (1σ) of duplicate analyses

As can be seen from Figures 3 and 4, and Table 1, helium release from the tungsten during the initial stepped-anneal tests was small compared to the total helium inventory. For W-2, the total ^{4}He released at 1600°C was only ~0.2% of the total ^{4}He. Similarly, for W-3, the ^{4}He released by 1200°C was only ~0.1% of the total.

Hydrogen Measurements

Hydrogen Analysis System

Hydrogen measurements initially conducted on the tungsten samples were accomplished using one of the analysis furnaces attached to the helium analysis system that had been extensively modified for the task. Details of the analysis setup were reported earlier *[5]*. This system was based on isotope-dilution, static-mode, gas mass spectrometry, similar to the method used for the helium measurements. Although this system provided useful initial data for the APT program, the system could only be used for relatively high hydrogen levels (thousands of appm), and the absolute accuracy of the system was difficult to assess. In particular, background hydrogen levels in the detector were difficult to determine.

In order to improve on the accuracy and sensitivity of the hydrogen measurements, a second development effort was undertaken which involved improvements to both the sample hydrogen extraction and detector components*[6]*. The hydrogen extraction system improvements involved significantly reducing the volume and type of materials in the sample furnace that were heated and in direct connection to the mass spectrometer detector. The detector improvements involved a complete redesign of the detector volume to minimize its size and its proximity to the extraction furnace. Also incorporated into the detector design was a chopper blade assembly to permit measurements using a modulated-beam (MB) technique. The MB technique involves chopping the input gas flow to the mass spectrometer, and then using a lock-in amplifier to detect the resulting modulated hydrogen signal. Although not used for the

present measurements, this technique is useful for situations where the background hydrogen levels in the detector volume are comparable or larger than levels being released from the analysis samples.

A schematic diagram of the hydrogen analysis system is shown in Figure 5. Hydrogen is extracted from the analysis samples by heating to temperatures up to ~1200°C. The extraction furnace shown on the left-hand side consists of a sample turntable assembly located above a ceramic test-tube- shaped crucible heated on the outside by a resistance-heated tungsten filament. The tungsten heating filament is contained inside a water-cooled copper enclosure connected to its own separate vacuum system. Samples are loaded into the upper section of the turntable and remotely dropped through the central vertical channel into the crucible using a bellows-sealed push rod.

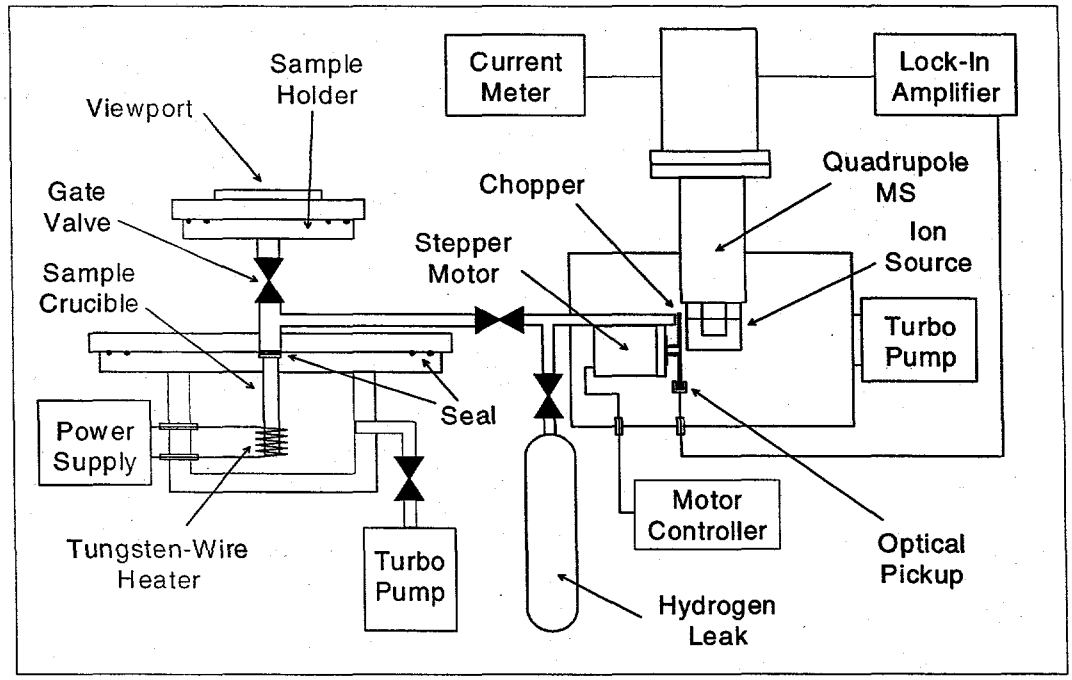

Figure 5 – *Hydrogen Analysis System*

The hydrogen detector system is shown in the right-hand side of Figure 5. Hydrogen gas flow from the extraction system travels through the horizontal vacuum line which terminates very near the ionization region of the quadrupole detector. The mass spectrometer detector is a quadrupole analyzer with an electron multiplier detector. For the present measurements, the output of the electron-multiplier was fed directly to a digital multimeter (DMM).

Calibration of the system sensitivity is accomplished using a hydrogen leak source attached to the vacuum line between the extraction furnace and the detector volume. The calibrated leak has a very small trapped volume, resulting in virtually no lowering of the leak rate with time. Calibration measurements are conducted before and after each sample analysis, and show an overall reproducibility of ~2 to 3%.

Measurements are also routinely conducted on specimens of a standard, hydrogen-containing steel maintained in the laboratory. The stated content of the steel is 5.2 ± 0.3 wppm. The average hydrogen content measured in more than 90 of these samples is 5.4

wppm with a reproducibility of ~30% (1σ). It is speculated that the variability observed in the standard samples is associated with actual heterogeneity in the hydrogen content at this small mass level.

Absolute uncertainty (1σ) in the hydrogen analyses is currently estimated at ~20%, and is due partly to the uncertainty in the calibrated hydrogen leak source. The system has been determined to be linear up to a total hydrogen release of at least 10^{17} atoms, which for a 0.5 mg steel sample, represents a hydrogen concentration of ~20,000 appm. Additional uncertainty may also be present from possible hydrogen release from remaining water layers or hydrated metal oxides on the surface of the sample that are subsequently dissociated by the hot crucible. It is hoped that with more experience with the system, this uncertainty will be reduced.

Retained Hydrogen in Tungsten

Using the new analysis system, hydrogen measurements were conducted on additional specimens from unirradiated control material and two of the irradiated tungsten samples from the original group of five samples prepared at LANL and reported earlier*[5]*, and on samples from two additional sets from LANL. Except for one sample which was analyzed using an approximate linear temperature ramp, all of the analyzes were conducted at a fixed crucible temperature of ~1200°C, which is the postulated off normal scenario for the APT design.

Hydrogen measurements are summarized in Table 2. Mean concentration and 1σ standard deviation in the replicate analyzes are given in the last column. Absolute uncertainty (1σ) in the hydrogen analyses is estimated at ~20%, and is due partly to the uncertainty in the calibrated hydrogen leak source discussed above. Additional uncertainty may also be present from possible hydrogen release from remaining water layers or hydrated metal oxides on the surface of the sample that are subsequently dissociated by the hot crucible.

Table 2 – *Retained Hydrogen in APT Tungsten*

Specimen	Mass[a] (mg)	Measured Hydrogen (10^{15} atoms)	Hydrogen Concentration (appm)[b] Measured	Corrected[c]	Average[d]
Unirradiated:					
W-blk	7.506	4.7	191	-	210
	10.22	7.8	233	–	±30
Irradiated:					
W-2	9.063	~42	~1400	~1190	1700
	1.526	10.2	2030	1820	±470
	3.282	25.0	2320	2110	
W-3	0.761	9.27	3710	3500	3500
1Wh	4.538	25.1	1680	1470	1990
	6.197	46.4	2280	2070	±480
	4.432	38.3	2630	2420	

1Wc	5.240	6.36	370	160	220
	4.390	7.23	502	292	±70
	3.719	5.18	424	214	

[a]Mass of specimen for analysis. Mass uncertainty is ±0.002 mg.
[b]Helium concentration in atomic parts per million (10^{-6} atom fraction) with respect to the total number of atoms in the specimen.
[c]Corrected for helium measured in unirradiated control material.
[d]Mean and standard deviation (1σ) of duplicate analyses.

As mentioned above, hydrogen release measurements with temperature were also conducted on one of the tungsten specimens, and are shown in Figure 5. The thin solid line in each graph is the crucible temperature profile as a function of heating time in seconds. Crucible temperature is given on the right hand y-axis. The thicker lines indicate the instantaneous hydrogen release in atoms per second on the left y-axis. Total heating time is given in the bottom axis of each graph.

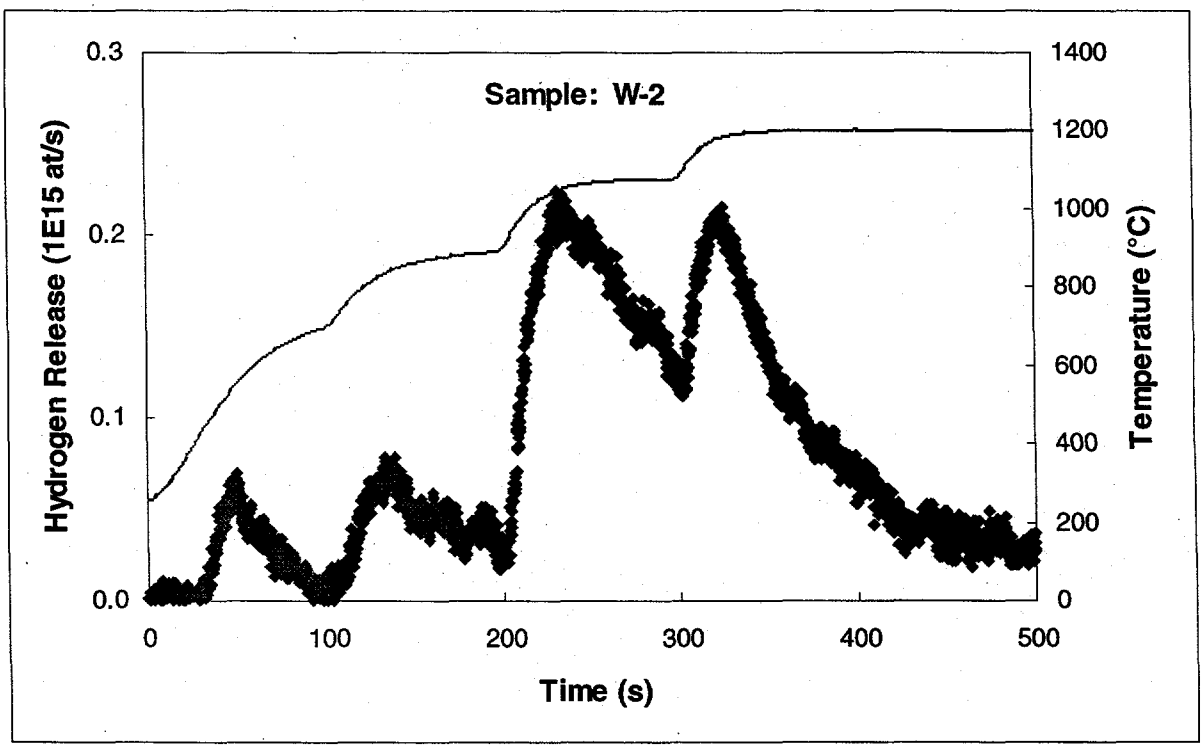

Figure 6 – *Hydrogen Release From Irradiated Tungsten at Temperatures Between 750°C and 1200°C*

LAHET Calculations of Helium and Hydrogen Content

A detailed Monte Carlo model of the APT materials irradiation has been completed at LANL using the LAHET Code System (LCS) *[7]*. The LCS is the neutronic tool used for the design of APT and the estimation of radiation damage parameters, such as DPA and gas production. Because the proton energy spectrum and beam profile vary

throughout the APT target/blanket (starting typically at 1.6 GeV), the measurement presented is prototypic for only one region of the target system. However, using the measurement as a calibration for the LCS will provide some insight into the accuracy of gas production predictions throughout the APT target/blanket.

Calculations of the helium and hydrogen production were carried out using the LCS. Details of the calculations have been presented in an earlier work *[5]*. Because the measured results are related to the total number of helium and hydrogen atoms that are stopped in the sample volume and not necessarily the production rate in the sample, the tally option used was IOPT=14 with charged particle transport turned on in LAHET (this is not the default LAHET option). The LCS default level density model was used with a pre-equilibrium model following the intranuclear cascade (not the LCS default). The results are summarized in Table 3 with a comparison to the average measured values. Statistical errors in the LCS calculations were less than 3%. Although the statistical errors in the LAHET calculations are small, overall uncertainty is expected to be about 50% for the prediction of radionuclides in general. This uncertainty estimate is based primarily upon the work of Ullmann, et al.*[8]*, who measured radioactive spallation products from tungsten and lead targets. The variation of predictive capabilities is large and seems, to some extent, to be a function of the target material *[8,9]*.

Table 3 - *Comparison of LCS Calculations With Measured Helium and Hydrogen Concentrations*

		Gas Concentrations (appm)					
	Location	Helium			Hydrogen		
Sample	(mm)[a]	Measured	Calculated	C/M[b]	Measured	Calculated	C/M[b]
W-2	9.5	754	760	1.0	1700	4980	2.9
W-3	9.0	715	760	1.1	3500	4980	1.3
1Wh	7.5	-	760	-	1990	4980	2.5
1Wc	65	23.9	-	-	220	-	-

[a]Sample location relative to beam center.
[b]Calculated-to-measured ratio.

Discussion and Conclusions

Helium release from two irradiated tungsten samples during stepped-anneal tests was small compared to the total residual helium inventory measured in the same samples. At 1200°C, which is the postulated off normal temperature for the APT project, the total helium release for one sample was only ~0.1%. At 1600°C, the total helium release in a second sample was only slightly higher at ~0.2%. Helium release was first observed at about 800°C. One sample showed some evidence for an increasing helium release with temperature between 800°C and 1400°C. At the highest temperatures reached, where multiple helium analyses were conducted, both samples showed evidence of a leveling off in the helium release. Helium-3 release for both samples was at or below the detection limit of the analysis system (~10^{12} atoms) for the particular setup used in these tests. Given the low quantities of helium release at 1200°C, it is unlikely that this release will result in any pressure buildup at the target/cladding interface of a production target.

Total helium concentrations measured in the two irradiated tungsten samples averaged 733 ± 28 (1σ) appm for the near beam center locations, and ~24 appm at 65 mm from beam center. Comparison with LAHET calculations gives C/M values of ~1.0 to 1.1 near beam center, to ~x.x away from the beam. As indicated previously *[5]* this close agreement, however, is likely fortuitous. Absolute uncertainty (1σ) in the helium contents is estimated to be between 1% and 2%.

New hydrogen measurements conducted on two unirradiated specimens of as-received tungsten material showed a low hydrogen impurity content of about 200 appm, in good agreement with the preliminary data obtained earlier *[5]*. New analyses of irradiated samples gave total hydrogen contents ranging from approximately 1700 up to 3500 appm, also in good agreement with earlier preliminary data.

Hydrogen release profiles with increasing temperature, in Figure 11, shows four release peaks at temperatures of approximately 550, 850, 1100, and 1200°C. Some of this change in hydrogen release is likely attributable to the nonlinearity in the temperature ramp, however, the data nonetheless suggest a variety of trapping sites for the hydrogen in the tungsten. Both the present analysis, and the earlier preliminary measurements suggest complete hydrogen release from the tungsten at temperatures of 1200° (or lower), within a few minutes. Whether or not this released hydrogen will result in a pressure buildup at the target/cladding interface of a production target will depend largely on whether or not any gaps exist between the tungsten and the cladding. If no gap exists, then the hydrogen will likely diffuse through the Alloy 718 at a rate equal to its release from the tungsten. If a gap exists, however, the hydrogen will likely recombine to form molecular H_2, and release through the cladding may be slow.

Comparison of the hydrogen values with LAHET calculations gives C/M values ranging from ~1.3 to 2.9. Some of the discrepancy between the calculated and measured values is the result of the uncertainties in the measurements and the calculations (about 50% each). Diffusional losses were not accounted for in the LAHET calculations.

Within the respective uncertainties of the gas measurements and calculations, several observations can be made:

- As expected, significant levels of helium and hydrogen were observed in the tungsten target material.
- Helium release at the postulated off normal temperature of 1200°C is small at about 0.1 to 0.2% of the total generated helium. Helium release first occurs at ~800°C, and the release rate does not change significantly with temperature.
- Given the small levels of helium released, helium gas buildup should not contribute significantly to any pressure buildup at the target/cladding interface of a production target.
- Hydrogen release was seen to occur in tungsten starting at ~500°C, with release peaks at ~550, 850, 1100, and 1200°C.
- The measurements suggest complete release of generated hydrogen within a few minutes at 1200°C. Whether or not this released hydrogen will contribute to a pressure buildup at the target/cladding interface will depend on whether there is a gap at the interface allowing recombination of the hydrogen into molecular form.
- LAHET calculations of gas generation in the target tungsten agreed reasonably with measurements within estimated uncertainties.

Acknowledgements

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