THERMAL RELEASE OF ^{3}He FROM TRITIUM AGED $LaNi_{4.25}Al_{0.75}$ HYDRIDE

Gregory C. Staack, Mark L. Crowder, and James E. Klein
Savannah River National Laboratory, Aiken, SC 29808; gregory.staack@srnl.doe.gov

Recently, the demand for He-3 has increased dramatically due to widespread use in nuclear nonproliferation, cryogenic, and medical applications. Essentially all of the world's supply of He-3 is created by the radiolytic decay of tritium. The Savannah River Site Tritium Facilities (SRS-TF) utilizes LANA.75 in the tritium process to store hydrogen isotopes. The vast majority of He-3 "born" from tritium stored in LANA.75 is trapped in the hydride metal matrix. The SRS-TF has multiple LANA.75 tritium storage beds that have been retired from service with significant quantities of He-3 trapped in the metal. To support He-3 recovery, the Savannah River National Laboratory (SRNL) conducted thermogravimetric analysis coupled with mass spectrometry (TGA-MS) on a tritium aged LANA.75 sample. TGA-MS testing was performed in an argon environment. Prior to testing, the sample was isotopically exchanged with deuterium to reduce residual tritium and passivated with air to alleviate pyrophoric concerns associated with handling the material outside of an inert glovebox. Analyses indicated that gas release from this sample was bimodal, with peaks near 220 and 490°C. The first peak consisted of both He-3 and residual hydrogen isotopes, the second was primarily He-3. The bulk of the gas was released by 600°C.

I. INTRODUCTION

The SRS Tritium Facilities (TF) has several $LaNi_{4.25}Al_{0.75}$ (LANA.75) hydrogen storage beds that have reached the end of their service life and have been removed from service. These beds were used to safely store tritium in hydride form. Tritium decays to He-3 with a half-life of approximately 12.3 years. When tritium is stored on LANA.75, the larger He-3 atoms "born" in the hydride become trapped and cause stresses in the metal crystal lattice. These stresses significantly decrease the reversible tritium storage capacity of LANA.75 over time, primarily through the formation of a "heel" of hydrogen isotopes that will not desorb under normal process conditions. Eventually the metal will become saturated and He-3 will begin to weep out of the hydride. When this begins, the LANA.75 bed will no longer be able to deliver He-3-free hydrogen isotopes. When either the bed begins to weep He-3 or the loss of reversible capacity adversely impacts process throughput, the hydride bed undergoes a series of isotope exchanges, is backfilled with an inert gas, and removed from service.

Retired beds contain significant quantities of He-3 (Ref. 1). This He-3 has applications in nuclear nonproliferation, cryogenic refrigeration, and medical imaging, among others. The SRS TF is interested in recovering He-3 from the retired beds by heating them under vacuum in the Tritium Extraction Furnace (TEF). Current understanding of He-3 release from tritiated LANA type materials is limited. Work performed at Mound on a LANA.3 sample with 21 months of tritium exposure shows limited He-3 release from the solid until approximately 850°C. Other work (Ref. 2) on LANA.75 with approximately 11.6 years of tritium exposure shows He-3 evolution below 450°C. This report documents the results of testing the thermal release of He-3 from a passivated, bench scale, tritium aged LANA.75 sample in an inert environment using TGA-MS (thermogravimetric analysis-mass spectrometry).

II. EXPERIMENTAL

II.A. Sample Information

The LANA.75 sample used for testing began tritium aging in March of 1987. Though the sample was subjected to periodic absorption and desorption testing, it remained tritium loaded the majority of the time. In January 2004 the sample was thermally desorbed at 185°C, reloaded with deuterium, and desorbed at 160°C with a final pressure of 4.07kPa. Beginning in May 2010, the sample underwent a series of deuterium exchanges to reduce the residual tritium content. The final hydrogen isotope concentration in the sample was 0.354 Q/M where Q is the number of hydrogen atoms (H, D, or T) and M is the number of metal atoms in the hydride. The hydrogen isotope concentrations, including trace hydrogen containing compounds, e.g. Q_2O or CQ_4, prior to passivation were 0.563% H, 83.90% D, and 15.53% T as measured by a high resolution mass spectrometer in the Tritium Facilities.

Following the exchange of deuterium for most of the tritium in the sample, the hydride was evacuated at ambient temperature and passivated. Passivation is the formation of a thin oxide layer on the surface of the reduced metal powder, rendering it insensitive to air. Passivation is typically accomplished by adding air to the

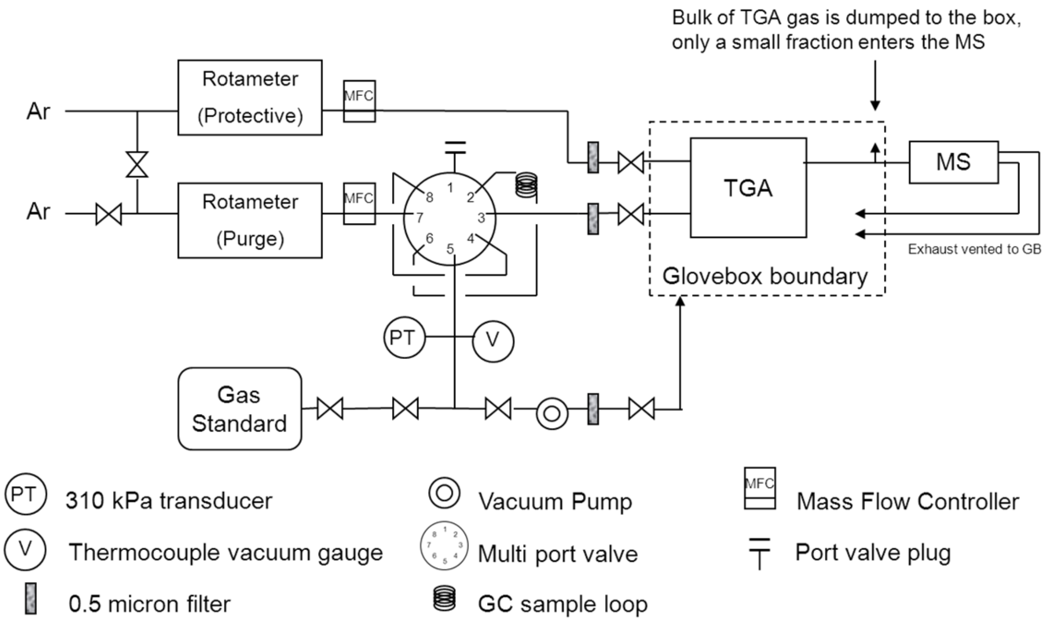

Fig. 1. Test Apparatus

sample in a controlled manner. Following passivation, several portions were recovered (Ref. 3). To further reduce tritium inventory and ensure worker safety, the sample was opened to the glovebox to offgas for a week before TGA-MS testing began.

II.B. Test Apparatus

The test apparatus consisted of a small gas manifold located outside of the glovebox, a TGA (Netzsch model 409 PC Luxx) located inside the air glovebox, and an MS (Pfeiffer Thermostar model GSD301T3) located outside the glovebox. Gas sampled by the MS was returned to the glovebox. A schematic of the apparatus is given in Fig. 1.

A manifold was constructed to deliver known amounts of standard gases to the MS and to provide consistent calibrated gas flow to the TGA. Protective and Purge flows to the TGA were 99.999% argon and were controlled via a pair of MKS Instruments Model 1179 mass flow controllers (MFCs). Rotameters (Vogtlin V100) installed upstream of the MFCs were used to verify that the MFC calibration did not drift during testing. Room temperature was measured using a Vaisala HM34 Humidity & Temperature Meter. Pressure was measured with a 0-310 kPa calibrated Paroscientific pressure gauge model 6000-45A. Finally, vacuum was measured using a Teledyne-Hastings Vacuum gauge, model SV-33.

II.C. Thermogravimetric Analyzer Calibration

Confirmation of the temperature calibration of the TGA (Netzsch model 409 PC Luxx) was performed by determining the melting point of five pure metals using the TGA Differential Scanning Calorimetry mode with a ramp rate of 10°C/minute. The melting points ranged from 156.6°C (Indium) to 1064.4°C (Gold). In all cases, the TGA measured melting points were within 2°C of literature values, so the factory-set temperature scale was accepted.

The TGA microbalance was initially calibrated via an internal calibration step available using the instrument software. Before and after testing of LANA.75 materials, the TGA was tested with gypsum standards of nominally 10-50 mg. Gypsum, (calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$)) loses both waters of hydration when heated to about 250°C, which equates to a theoretical weight loss of 20.93 wt %. Gypsum test results performed before and after LANA.75 tests were within 2% of the theoretical value.

II.D. Mass Spectrometer Calibration

The MS was calibrated for helium-4 and deuterium by introducing known volumes of each standard gas mix to the TGA Purge gas upstream of the instrument via gas chromatography sample loops. These loops were connected to the Valco Multi port valve as shown in Fig 1. Standard gas mixes were either 39.77 mol % He-4 in argon or 18.81 mol % D_2 in argon, and both were prepared using the calibrated Paroscientific pressure gauge mentioned above. Calibrations were performed using argon for both the Protective and Purge flows at 0.076 and 0.127 Pa*m^3/s, respectively. Previous work demonstrated that He-4 and He-3 have essentially identical MS responses over a wide pressure range, permitting the sensitivity factor for He-4 to be used to quantify He-3. Responses for standard gases were normalized against Ar-36 and integrated over time. The resulting calibration curves showed very good linearity throughout the tested range with R^2 values greater than 0.99.

II.E. Method

A series of scoping tests using non-tritiated LANA.75 material were performed to identify the argon flow rates, purge times, and TGA ramp rates necessary to achieve <1 weight percent mass increase due to sample oxidation for the duration of the test. A portion of the tritiated LANA.75 sample was placed in a fired (recently heated to 1000°C) alumina crucible and weighed using the TGA balance. The weight was recorded and the balance tared. The TGA was swept overnight with argon to remove as much oxygen as practical. Testing was performed with Protective and Purge flows set to 0.076 and 0.127 Pa*m^3/s, respectively. The sample was heated at 15°C/min to approximately 1000°C and the TGA results were buoyancy corrected. The MS monitored the TGA effluent at mass-to-charge ratios of 2, 3, 4, 5, 6, 18, 19, 20, 21, 22, 28, 32, and 36, though calibrations can only be claimed for D_2 and He-3. Responses for samples were normalized against Ar-36 and integrated over time using the trapezoid rule.

III. RESULTS AND DISCUSSION

MS results clearly demonstrated the evolution of helium and various hydrogen isotopes in a bimodal manner as shown in Fig. 2. The first peak consisted of both helium and hydrogen, where the second peak was predominantly helium. Virtually no additional gas was desorbed above 600°C.

Negligible changes in mass-to-charge ratios of 28 and 32 were observed. Small deflections in masses 18-22 were observed, corresponding to the various isotopologs of water. The fact that a peak was observed for mass 20 in spite of the high background associated with doubly ionized Ar suggests that a significant amount of D_2O evolved from the sample as shown in Fig. 3. The D_2O was likely formed on the hydride surface either during passivation activities or by reduction of the oxidized surface layer of the hydride as the heel was desorbed. Heating liberated sorbed waters from the sample surface.

For estimating purposes, the MS response for deuterium was applied to other hydrogen isotopologs. This was not believed to produce substantial errors because deuterium had been demonstrated via high resolution MS to be the principal hydrogen isotope present. Other samples suggested that the the lower temperature mass 3 peak may be two separate peaks evolving almost simultaneously. It is not known whether this is the result of small amounts of HD desorbing from the sample or He-3 depopulating trap sites of similar energies. Because minimal protium was detected, the entire mass 3 trace was attributed to He-3, though some HD was likely present. Similarly, the mass 4 peak in Fig. 2 was attributed to D_2, though trace HT was likely present. No attempt was made to quantify hydrogen that evolved as oxide. Normalized TGA-MS hydrogen isotope results were in good agreement with the final deuterium exchange gas sample analyzed with the high resolution MS in the Tritium Facilities and are shown in Table I.

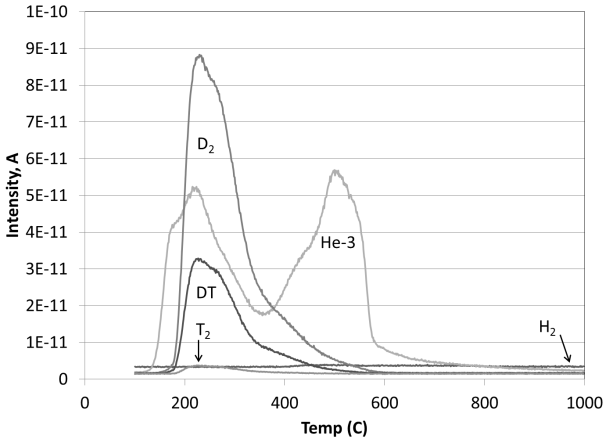

Fig. 2. MS results of evolved hydrogen

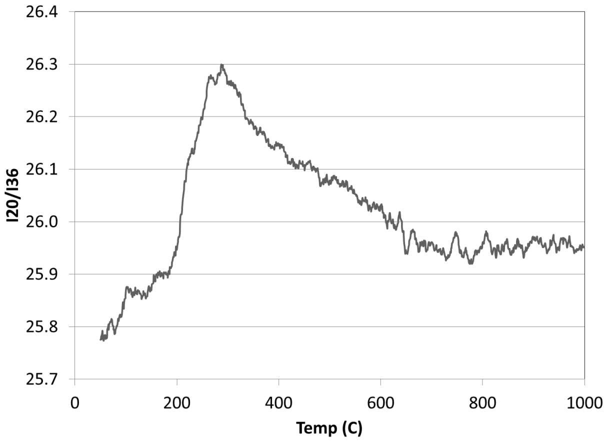

Fig. 3. MS results indicating evolution of D_2O

TABLE I. Comparison of High Resolution and TGA-MS Elemental Hydrogen Results

Mass	TF High Resolution Results	TGA-MS Peak Areas
2 (H_2)	Not Detected	0.32
4 (D_2, HT)	71.37	72.73
5 (DT)	26.07	25.31
6 (T_2)	2.56	1.65

The derivative of the TGA results over the course of the experiment was smoothed and corroborates the results observed by the MS as shown in Fig. 4. At temperatures above approximately 600°C, the figure shows the sample weight increased slightly, likely due to oxidation. Mass gains of less than 1% were also observed with other samples. For comparison, a non-tritiated LANA.75 sample tested in air was shown to increase in weight by approximately 26%.

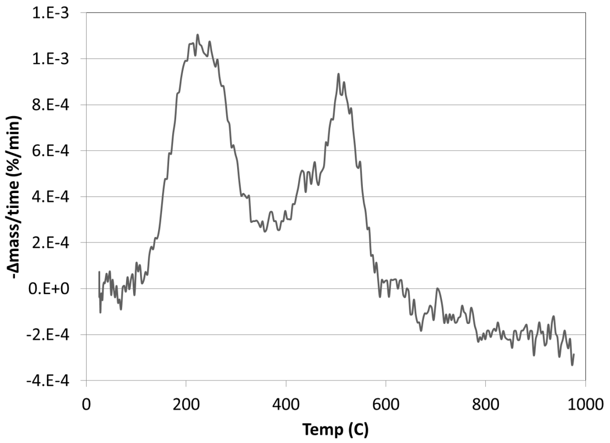

Fig. 4. TGA results

A summary of the gas removed from the sample is given in Pa*m^3/kg and gas to metal atomic ratios in Table II. The total calculated amount of He-3 released was considerably less than what was expected to be in the sample. A He-3 to metal atomic ratio of 0.35 had been estimated to be the approximate saturation point for LANA type hydrides; this sample had sufficient tritium exposure to achieve that value. In addition, the total hydrogen observed by the MS was 28-29% of that calculated during heel exchange operations. The differences in both of these values may be due to losses during sample passivation; an oxidized metal hydride will retain neither hydrogen nor helium. If substantial He-3 was still present in the sample, temperatures in excess of 1000°C or an alternate approach would be needed to recover the remaining gas.

TABLE II. Measured Gas Quantities and Loadings

Mass	**Pa*m^3/kg LANA.75**	**Atomic gas/metal ratio**
2 (H_2)	5.37	-
3 (He-3)	3300	0.100
4 (D_2, HT)	1200	0.072
5 (DT)	434	0.026
6 (T_2)	28.2	0.002
Total Q_2	1670	0.101

IV. CONCLUSIONS

TGA-MS analysis of tritiated LANA.75 gave fairly reproducible results with respect to mass change and effluent gas composition. Integration of the areas produced by TGA-MS gave hydrogen isotope concentrations very similar to those measured by the high resolution MS in the TF. This confirmed that negligible amounts of protium were in the sample, allowing the entire mass 3 peak to be attributed to He-3 instead of partitioning it between He-3 and HD.

Heating the sample to 1000°C indicated two primary regions of gas release, one near 220°C and the other near 490°C as indicated by both the TGA and MS. Both the amounts of He-3 and total hydrogen observed by the MS during testing were 28-29% of the expected values. This discrepancy is likely due to oxidation of the sample during passivation activities and allowing the sample to offgas before it was tested. It is believed that oxidized LANA.75 is incapable of retaining either hydrogen isotopes or He-3.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Tommy Sessions for preparation of the gas standards, Patrick Westover for his assistance modifying the system process lines upstream of the TGA, David Blair for high resolution mass spectrometry analysis, and finally Roger Pilgrim and Janice Rice for their help exchanging, passivating, and harvesting the sample.

This paper was prepared in connection with work performed under Contract No. DE-AC09-08SR22470 with the U. S. Department of Energy.

REFERENCES

1. R. T. WALTERS and W. C. MOSLEY, “Tritium Storage Effects on La-Ni-Al Alloys: Helium and Tritium Trapping”, USDOE Interoffice Memorandum, DPST-88-498, *Storage Science Meeting*, Los Alamos, NM, April 4-6 (1988).
2. K. L. SHANAHAN, “^{3}He Recovery from a Tritium-aged LANA75 Sample (U)”, USDOE Interoffice Memorandum, SRNL-STI-2010-00451, Savannah River Site, Aiken, SC, 29808, December 1 (2010).
3. G. C. STAACK, “Recovery of a Tritiated LANA Sample for Dose Conversion Factor Determination”, USDOE Interoffice Memorandum, SRNL-STI-2010-00748, Savannah River Site, Aiken, SC, 29808, November 24 (2010).