Conf-910920--28

WSRC-MS--91-017

DE92 010061

TRITIUM MEASUREMENT TECHNIQUE USING "IN-BED" CALORIMETRY (U)

by

J. F. Klein, et al

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

A paper proposed for presentation at the
Fourth ANS Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications
Albuquerque, New Mexico
September 30-October 4, 1991

and for publication in the proceedings

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TRITIUM MEASUREMENT TECHNIQUE USING "IN-BED" CALORIMETRY*

J. E. Klein**, M. K. Mallory, and A. Nobile, Jr.
Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

ABSTRACT

One of the new technologies that has been introduced to the Savannah River Site (SRS) is the production scale use of metal hydride technology to store, pump, and compress hydrogen isotopes. For tritium stored in metal hydride storage beds, a unique relationship does not exist between the amount of tritium in the bed and the pressure-volume-temperature properties of the hydride material. Determining the amount of tritium in a hydride bed after desorbing the contents of the bed to a tank and performing pressure, volume, temperature, and composition (PVTC) measurements is not practical due to long desorption/absorption times and the inability to remove tritium "heels" from the metal hydride materials under normal processing conditions. To eliminate the need to remove tritium from hydride storage beds for measurement purposes, an "in-bed" tritium calorimetric measurement technique has been developed. The steady-state temperature rise of a gas stream flowing through a jacketed metal hydride storage bed is measured and correlated with power input to electric heaters used to simulate the radiolytic power generated by the decay of tritium to ^3He. Temperature rise results for prototype metal hydride storage beds and the effects of using different gases in the bed are shown. Linear regression results shows that for 95% confidence intervals, temperature rise measurements can be obtained in 14 hours and have an accuracy of ± 1.6% of a tritium filled hydride storage bed.

INTRODUCTION

Tritium, a radioactive isotope of hydrogen, is normally stored in production facilities in stainless steel tanks at low gas pressures to minimize the potential for release to the environment. At the Savannah River Site, metal hydride technology will be used to store, purify, isotopically separate, pump, and compress hydrogen isotopes[1]. Nuclear material inventories need to be performed on a periodic basis and tritium inventories in tanks can be determined easily by pressure-volume-temperature-composition (PVTC) measurements. For metal hydride applications, a new method was needed to determine tritium inventories for metal hydride storage beds: stainless steel process vessels containing metal hydride powders for storing hydrogen isotopes.

After extended periods of tritium exposure, La-Ni-Al metal hydride materials to be used in the storage beds develop tritium "heels"[2]: residual tritium which cannot be removed by heating and evacuating the gas from the metal hydride bed. The inability to desorb all the tritium from the hydride bed led to developing "in-bed" tritium inventory methods: methods where the tritium remains in the metal hydride bed during inventory measurements.

The objectives for the in-bed measurement technique were to 1) account for the tritium without removal of the gas from the hydride bed, 2) determine the amount of tritium in the metal hydride bed when a mixture of hydrogen isotopes are stored in the bed, 3) have a simple measurement system, 4) have sufficient accuracy in the calculated tritium inventory, and 5) conduct the measurement in a reasonable amount of time. To do this, calorimetry techniques were developed based on the constant, radiolytic power generated by the decay of tritium to ^3He. To simulate tritium stored in a metal hydride bed, electric heaters were used to simulate the radiolytic

---

*The information in this article was prepared during the course of work under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

**Author to whom all correspondence should be addressed.

decay energy and protium was used as the hydriding isotope.

IN-BED CALORIMETRIC OPTIONS

Two different in-bed calorimetric methods were tested for development. The static gas method correlated the initial rate of pressure increase of a gas in a jacket surrounding a metal hydride bed with the amount of simulated tritium in the bed. The flowing gas method correlated the steady-state temperature rise of a constant flow rate gas stream as it passed through an annular jacket surrounding a metal hydride bed with the amount of simulated tritium in the bed.

The static gas method was a fast, transient measurement technique, but the results obtained varied with the number of absorption/desorption cycles the metal hydride had experienced. For constant simulated tritium power levels, the results also varied when the composition of gases in the metal hydride bed varied[3]. The variation in the results for the static gas method with metal hydride cycling history and gas composition led to the development of the flowing gas method.

MODELING

The metal hydride bed in Figure 1 has internal power generation Q, is jacketed, is externally insulated, and has gas flowing through the annulus of the bed at rate W SLPM. The energy balance for the hydride bed is given by

$$Q = W C_p K_W \Delta T + UA \Delta T_{UA} \qquad (1)$$

where K_W converts W to mass flow rate, $\Delta T = T_o - T_i$, T_o is the outlet gas temperature, T_i is the inlet gas temperature, C_p is the average heat capacity of the gas between T_o and T_i, UA is the product of an average overall heat transfer coefficient and the heat transfer area, ΔT_{UA} is defined in the following paragraphs. In Equation (1), $WC_pK_W\Delta T$ represents the energy carried away by the flowing gas, while $UA\Delta T_{UA}$ accounts for the energy exchanged with the surroundings at temperature T_s.

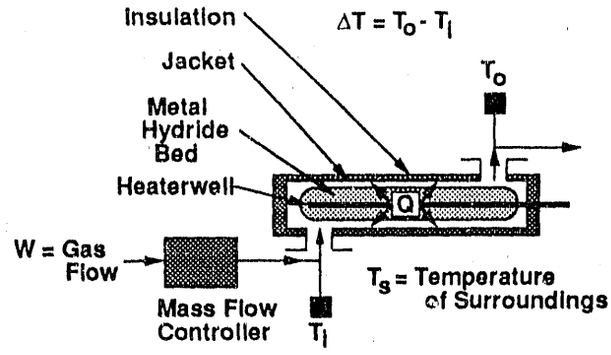

Figure 1. Metal Hydride Bed Flowing Gas Calorimeter.

In the case where $T_i \approx T_s$, the average temperature difference between the flowing gas stream and T_s is used for ΔT_{UA}: $\Delta T_{UA} = \Delta T_{ave}$ where

$$\Delta T_{ave} = \frac{(T_o - T_s) + (T_i - T_s)}{2} \approx \frac{(T_o - T_i) - 0}{2} = \frac{\Delta T}{2} \qquad (2)$$

In the case where $T_i \neq T_s$, the log-mean temperature driving force is used for ΔT_{UA}: $\Delta T_{UA} = \Delta T_{lm}$ where

$$\Delta T_{lm} = \frac{[(T_o - T_s) - (T_i - T_s)]}{\ln[(T_o - T_s)/(T_i - T_s)]} = \frac{\Delta T}{\ln[(T_o - T_s)/(T_i - T_s)]} \qquad (3)$$

Factoring out ΔT, the energy balance can be written as

$$Q = \left[W C_p K_W + \frac{UA}{K_{UA}} \right] \Delta T \qquad (4)$$

where $K_{UA} = 2$ for $T_i \approx T_s$ and $K_{UA} = \ln[(T_o - T_s)/(T_i - T_s)]$ for $T_i \neq T_s$.

The T/M ratio for a metal hydride bed is a convenient way of expressing the amount of tritium absorbed or "loaded" into a metal hydride. T/M is the atomic ratio of tritium atoms per atom of metal in the metal hydride material.

The conversion constant K_T is used to relate T/M to Q and is defined by $Q = K_T \times T/M$. Using the definition of K_T and Equation (4), ΔT can be expressed as a function of T/M:

$$\Delta T = \frac{K_T}{\left[W C_P K_W + \frac{UA}{K_{UA}}\right]} (T/M) \qquad (5)$$

If C_P and UA are independent of T/M, T_i, T_o and T_s, a plot of ΔT versus T/M can be represented by a straight line. Since electric heaters were used to simulate the radiolytic power generated by the decay of tritium, T/M represents the power dissipated by the electric heaters and is referred to as the simulated tritium bed loading.

EXPERIMENTAL

The hydride bed used for the experiments were two prototype production scale metal hydride beds fitted with longitudinal heaterwells, jacketed, and insulated with cellular glass insulation with an aluminum covering. An uninsulated expansion volume was connected to each hydride bed for pressure protection of the beds as they were heated during the experiments.

The metal hydride material used was a $LaNi_{4.25}Al_{0.75}$ alloy purchased from Ergenics, Inc.[4] The hydride material was poured into the hydride bed, distributed within the bed, and x-rayed to verify the material was distributed evenly along the length of the bed. The hydride material was activated by heating and evacuating the bed, and then exposing the hydride to protium.

A pressure regulator supplied compressed air to a manifold of mass flow controllers (MFCs) which was used to flow compressed air through the jackets of the metal hydride beds. The pressure in the jackets of the beds was controlled by back-pressure regulators downstream of the beds. A circulation heater was installed in the MFC manifold and supplied heated air to one of the beds. Bed inlet and outlet temperature measurements were measured using four-wire RTD probes installed in thermowells in the compressed air piping near the flanges of the beds.

For experiments using protium, a calibrated volume was used to load protium into the hydride bed to the desired bed loading: expressed as the atomic ratio H/M. H/M values were calculated at ambient bed temperatures and T/M values were taken equal to these values. From these T/M values, heater power levels were calculated. For experiments using helium, the beds were evacuated, brought to room temperature, and filled with helium to approximately 780 torr. Target T/M values were chosen and heater power levels calculated.

Experiments were conducted by loading the beds with the desired gas, setting the flow rates of the MFCs, and setting the heater power levels to the power levels calculated from the T/M values. Data were collected at ten minutes intervals for 16 to 48 hours using a Hewlett Packard 3852A Data Acquisition and Control Unit with a Hewlett Packard Industrial Vectra® Computer.

RESULTS

The standard deviation of ΔT over a two hour time span of less than 0.15 K for at least one hour was the criteria used to determine the steady-state temperature rise of the gas. Steady-state ΔT data were usually obtained within 16 to 18 hours from the start of the experiment, but sometimes took longer to ascertain due to temperature fluctuations in the laboratory.

Baseline experimental conditions used for comparison of results were 1) bed inlet gas temperature at ambient conditions, 2) bed gas jacket pressure approximately 760 torr, and 3) gas flow rate of 70 SLPM.

1. ΔT Versus T/M for Different Beds

ΔT results for bed 1 and bed 2 with helium versus T/M are shown in Figure 2. The helium data for bed 1 and bed 2 shows a linear relationship for both beds with slopes that differ for the two beds by 11%. Since gas temperature rise results for the two beds are similar, only the results for bed 1 will be presented in the remainder of the paper.

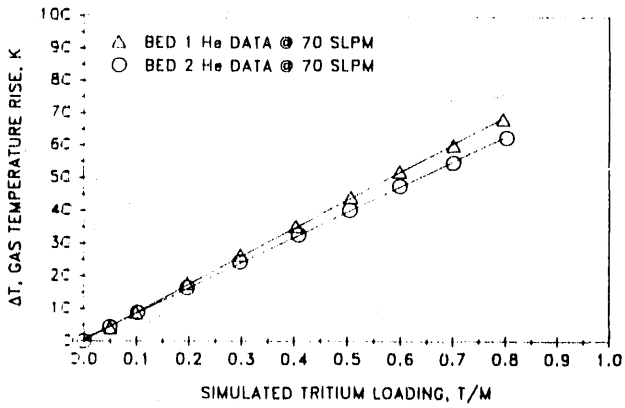

Figure 2. ΔT Versus T/M For Bed 1 and Bed 2 Helium Experiments.

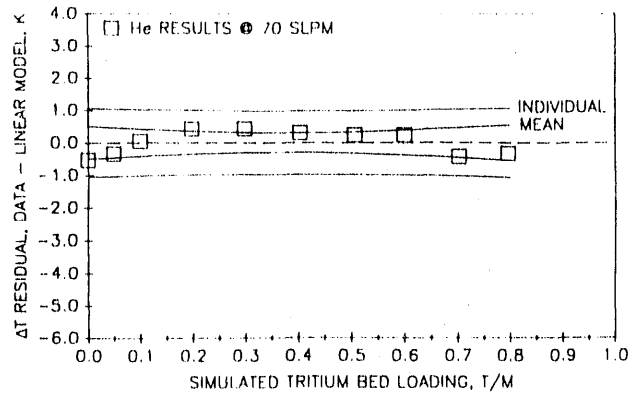

Figure 3. ΔT Residuals and 95% Confidence Intervals For Bed 1 Helium Experiments.

2. Helium Residuals and Confidence Intervals

A linear equation was calculated for the bed 1 helium ΔT versus T/M data shown in Figure 2 and residual errors were calculated using ΔT(experimental) - ΔT(linear regression) and plotted versus T/M in Figure 3. 95% confidence intervals were calculated for these data for individual and mean values of ΔT[5] and are also plotted as residuals in Figure 3. These results show that a quadratic equation may be a better model for the data, but the fact that all data are within the 95% confidence interval for an individual value was considered acceptable for our purpose of correlating ΔT with T/M.

3. Protium Residuals and Pressure Effects

ΔT residuals for experiments using protium in the beds were calculated relative to the linear regression equation for the helium data. ΔT residuals for protium experiments run after cycling the hydride material one to two times are shown in Figure 4. The results from Figure 3, as well as ΔT residuals for protium experiments repeated almost one year after the start of the experimental program are also shown in Figure 4. The results show that for T/M ≤ 0.7, ΔT residuals are within the 95% confidence intervals for an individual value and only depend only on T/M and not on the gas contained within the hydride bed.

After measuring the steady-state ΔT for the experiment at T/M = 0.83, two additional experiments were performed on the warm bed to determine the effect of external and internal heat transfer resistances. First, the gas pressure in the jacket of the hydride bed was increased to approximately 4000 torr and ΔT was measured at steady-state. After measuring ΔT, the pressure in the jacket of the hydride bed was returned to near 760 torr and then the pressure in the bed was decreased to approximately 4000 torr by bleeding protium from the bed. The results for these two experiments are plotted as residuals in Figure 4 and show the effects of external and internal bed pressure on ΔT.

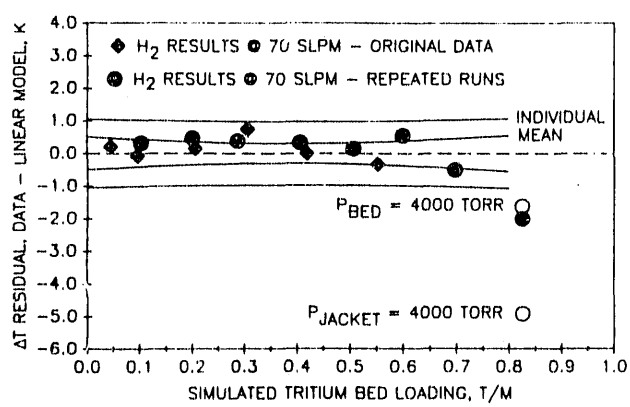

Figure 4. ΔT Residuals For Bed 1 Protium Experiments.

4. ΔT Time to Reach 95% Confidence Interval

In a production environment, it is desirable to know the time required to obtain reliable ΔT data of sufficient accuracy. To determine this time, experiments were conducted in which the bed was loaded with protium, cooled with the flowing gas to ambient conditions, the heaters turned on, and ΔT data collected for 24 hours. ΔT residuals at different times and at steady-state conditions for these experiments are shown in Figure 6. As can be seen from Figure 6, at least 14 hours are needed to ΔT results within a 95% confidence interval for an individual value.

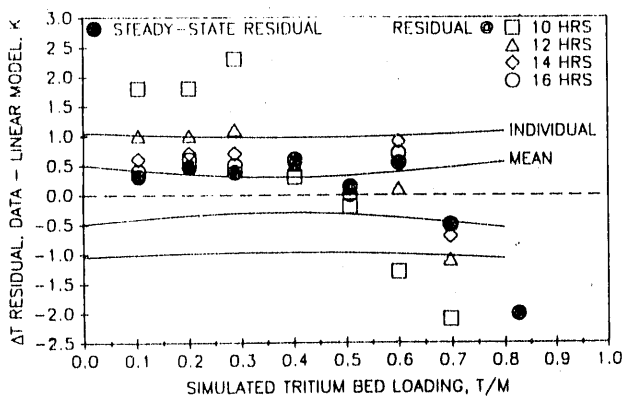

Figure 5. ΔT Residuals at Different Times for Bed 1 Protium Experiments.

5. Effect of Gas Flow Rate

To determine the effect of gas flow rate on ΔT, experiments were conducted using protium and gas flows of 50, 60, 70, and 80 SLPM. The ΔT versus T/M results for these experiments are shown in Figure 6. Linear equations were fit to the data and UA values calculated using Equation (5). The results of using Equation (5) are shown as straight lines in Figure 6 using the helium regression intercept of 0.14 K.

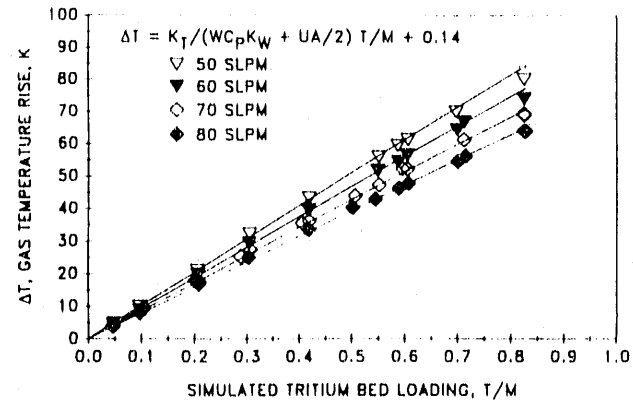

Figure 6. ΔT Versus T/M For Bed 1 Protium Experiments Using Different Gas Flow Rates.

DISCUSSION

The results in Figure 4 show that a linear model is adequate for correlating the ΔT versus T/M data for T/M up to 0.7. Above T/M = 0.7, the protium data deviate significantly from the linear model.

The heat transfer coefficient for the gas in the jacket of the hydride bed is the major resistance to heat transfer for the conditions tested and depends upon the flowing gas pressure and flow rate. Using the slopes of the ΔT versus T/M data from Figure 6 for T/M ≤ 0.7 and Equation (5), UA was calculated as a function of flow rate. UA was found to decrease 17% as the flow rate increased from 50 to 70 SLPM while UA had the same value at 80 SLPM as it had at 70 SLPM. The decrease in UA as gas flow rate increases is attributed to having a cooler hydride bed and less natural convective heat transfer at higher flow rates.

The internal bed pressure has some effect on ΔT measurement, but was not a significant factor for T/M ≤ 0.7. The bed pressure for the helium experiments shown in Figure 5 was approximately 790 torr, while the bed pressure for the protium experiments varied from 45 to 2030 torr for T/M between 0.1 and 0.7. For protium experiments above 0.7 T/M, the bed pressure increased greatly and had a measurable effect on ΔT measurements.

To determine the effect of temperature on UA, experiments were conducted at T/M = 0.42 and 70 SLPM with inlet air temperatures ranging from 23 to 80 °C. Using Equation 5 and $\Delta T_{UA} = \Delta T_{lm}$, UA was calculated at different inlet temperatures. UA was found to be independent of T_i and similar to the value calculated at 70 SLPM from the slope of the ΔT versus T/M data.

To apply the flowing gas calorimetric technique to determining tritium inventories in production scale metal hydride beds, steady-state ΔT measurements, at a constant gas flow rate, need to be measured for a hydride bed filled with various amount of tritium. Once this bed "calibration" data has been obtained, a linear regression is performed on the data.

The tritium inventory in the bed is determined by measuring ΔT and using the calibration data regression to obtain the amount of tritium in the bed: this procedure is called inverse regression. The inverse regression variance in calculating T/M is a sum of systematic and random errors and was calculated for the helium data shown in Figure 3[6]. For T/M between 0 and 0.8, the standard deviation in calculating T/M had a maximum variation of 11% with a maximum value of ± 0.0054 T/M at T/M = 0.8. 95% confidence intervals give the uncertainty in determining T/M using this technique of ± 0.011 T/M. For a full metal hydride bed loading of T/M = 0.7, this represents a 1.6% full bed measurement error.

CONCLUSIONS

The flowing gas calorimetric technique allows the determination of tritium inventories in a metal hydride bed by measuring the steady-state temperature rise of a gas stream flowing through the annular jacket of a metal hydride bed. For bed loadings up to T/M = 0.7, ΔT measurements are independent of gas pressure and composition within the hydride bed. After obtaining ΔT versus T/M calibration data for the bed, tritium inventories within the bed can be determined within 95% confidence levels within 14 hours with an accuracy of ± 1.6% of a tritium filled metal hydride storage bed.

ACKNOWLEDGEMENTS

The authors would like to thank W. L. Moyer who collected a large portion of the experimental data for this report.

REFERENCES

1. M. S. Ortman, L. K. Heung, A. Nobile, and R. L. Rabun, III, J. Vac., Sci. Technol., A8(3), 2881 (1990).

2. R. T. Walters, J. Less-Common Met., 157, 97 (1990).

3. A. Nobile, Jr., Savannah River Laboratory, private communication, (1987).

4. E. Lee Houston, Ergenics, Inc. 681 Lawlins Road, Wyckoff, NJ 07481.

5. N. Draper and H. Smith, "Applied Regression Analysis", 2nd ed., Chap. 1 (1981).

6. J. L. Jaech, "Statistical Methods in Nuclear Materials Control", Chap. 3 (1973).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

DATE
FILMED
5/08/92