Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

INERT BLANKETING OF A HYDRIDE BED USING TYPICAL GRADE PROTIUM

J. E. Klein

Savannah River National Laboratory: Aiken, SC 29808, james.klein@srnl.doe.gov

The reduction in hydride absorption rate due to "blanketing" can be explained in terms of a reduced hydrogen partial pressure in the bed due to the accumulation of inerts (i.e. non-hydrogen isotopes) in the bed void volume. Literature results show reduced absorption rates when protium for bed absorption contains helium with low-end inert compositions in the 0.6 to 1% range.

A hydride bed containing 9.66 kg of $LaNi_{4.25}Al_{0.75}$ (LANA0.75) metal hydride - a nominal capacity of 1400 STP-L, was cycled repeatedly to decrepitate the hydride material into smaller particles for bed strain measurement. The hydride cycles added and removed nominally 1000 to 1100 STP-L of protium per hydride cycle. Consistent and repeatable absorptions results were observed for different absorption cycles.

During one of the absorption tests, slower absorption results were obtained due to the use of typical grade (500 ppm inerts), instead of research grade, protium which blanketed the bed. The impact of 0.05% inerts in protium on bed absorption rate is shown and explained in terms of an increase in inert partial pressure as the bed was loaded.

I. INTRODUCTION

The absorption rate of hydrogen isotopes for a process metal hydride bed can be greatly inhibited by the presence of inerts (non-hydrogen isotopes) in the bed. The inerts can come from sources external to the bed (i.e. non-hydrogen isotopes in the supply gas to be absorbed by the bed) or sources internal to the bed (i.e. He-3 from gas phase tritium decay[1] or He-3 released from a hydride material during gas absorption.[2]) Theories postulated about He-3 releases during hydride absorption include localized heating of a low pressure hydride (like depleted uranium) which releases the He-3 due to the temperature increase while another is the hydride phase or crystal structure changes (e.g. body centered cubic to hexagonal close packed) during hydride absorption which releases He-3.

Independent of He-3 release from metal tritides, inerts in the gas supplied to a hydride bed can impede bed absorption rate by the accumulation of these inerts in the void space of the bed. One solution to minimize the impact of inerts on bed absorption is to create a flow-through bed design to remove inerts from the bed and thus allow continued bed absorption.

Experiments on the effect of inerts on absorption rates have been performed with Pd on kieselguhr (Pd/k) using 1% to 67% helium[3] and with 0.6% to 4% helium for depleted uranium[4]; although much lower impurity levels are known to impact measured hydride absorption pressures.[5] This paper describes the impact of 500 ppm (0.05%) impurities in protium on the absorption rate of a 9.66 kg $LaNi_{4.25}Al_{0.75}$ (LANA0.75) metal hydride bed.

II. BACKGROUND

The reduction in the hydride absorption rate of a metal hydride bed due to inerts can be explained by a decrease in hydrogen partial pressure in the bed due to the accumulation of the inerts in bed void space. As a gas supply is introduced to a hydride bed, hydrogen is removed from the gas phase by the hydride while the inerts accumulate in the void space of the bed. The gas pressure in the bed void space is a combination of three terms: the partial pressure of inerts initially in the bed (or released from the hydride), the partial pressure of hydrogen, plus the partial pressure of the inerts from the supply gas which accumulate in the bed void space.[5]

As inerts accumulate in the bed void space during absorption, there is a corresponding decrease in the partial pressure of hydrogen. The bed absorption rate is driven by the difference in hydrogen partial pressure between the gas in the bed void space and that of the hydride. As inerts accumulate in the bed void space, the partial pressure difference for absorption decreases resulting in reduced absorption rates. For larger concentrations of inerts in the supply gas increases, the faster the inert partial pressure in the bed void space will increase which produces lower absorption rates.

III. EXPERIMENTAL

The details of the hydride bed used in these tests has been described elsewhere.[6] A schematic and photo of the

bed, referred to as Stress Bed 01 (SB-01),[7] are shown in Fig. 1. The bed contained 9.66 kg of Ergenics Hy-Stor 201® LaNi4.25Al0.75 (LANA0.75) metal hydride.

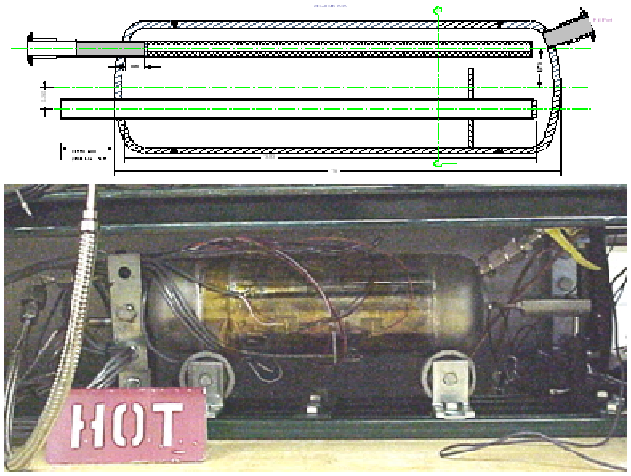

Fig. 1. Schematic and Photo of Stress Bed 01 (SB-01)

Figure 2 shows a simplified schematic of the test manifold. The system contained four hydrogen supply tanks totaling 188 L. To start an absorption test, these takes were initially filled to nominally to 989 kPa (7420 torr) with research grade hydrogen (99.995 % protium) from a compressed gas cylinder. The pressure regulator (PR) was set to approximately 333 kPa (2500 torr) to step down the pressure to the mass flow controller (MFC) which was used to measure gas absorption rate. To start the absorption test, the valve isolating the SB-01 from the manifold was opened.

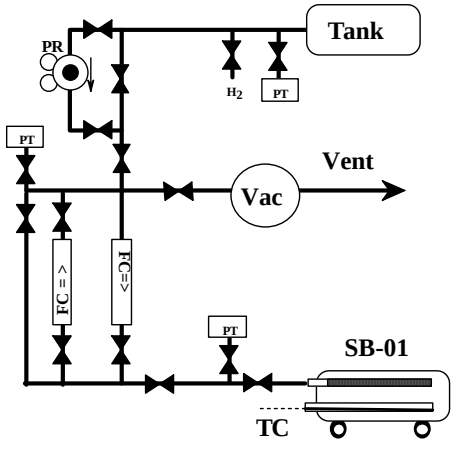

Fig. 2. Test Manifold Schematic

After the target amount of gas had been absorbed by the bed, the bed isolation valve was closed and final tank pressure readings were taken for gas absorption calculations. The bed was then heated and desorbed with the desorption rate measured by another MFC backed by a vacuum pump. When the target quantity of gas had been desorbed from the bed, the bed was isolated and cooled to ambient temperature, circa 22 to 24°C, before the start of the next absorption cycle. Nominally 1000 to 1100 STP-L were absorbed and desorbed per cycle.

IV. RESULTS

Fig. 3 shows the repeatability of the tests for SB-01 absorption Cycle 7 and Cycle 8: Cycle 7 results are shown as dotted symbols and Cycle 8 results shown as solid lines. The bed pressure, bed temperature as measured by a thermocouple in the bed's heater cartridge (TC05 in Ref. 7), and absorption flow rate data virtually over-lay one another for these two cycles.

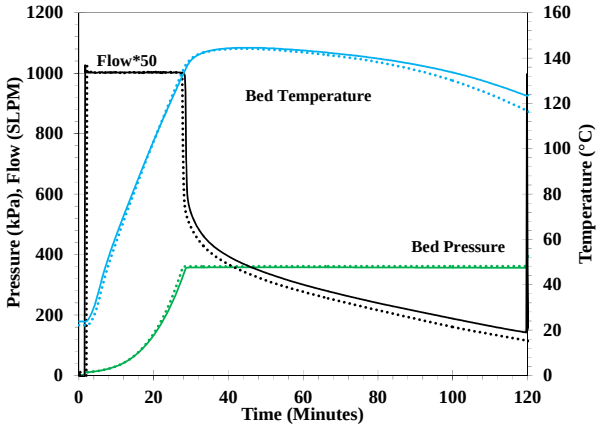

Fig. 3. SB-01 Absorption Cycle 7 (dotted) and Cycle 8 (solid) Results

The initial bed absorption rate is limited by the 20 SLPM range of the MFC. As the bed temperature increases due to the energy released during the absorption process, the absorption rate decreases due to the bed pressure reaching the pressure regulator delivery pressure. The absorption rate is then limited by the energy removal rate from the bed.

Fig. 4 shows the SB-01 absorption results for Cycle 8 and Cycle 9 (dashed lines). The figure shows the bed pressure increased faster for Cycle 9 under the same test conditions. Since the bed pressure in the Cycle 9 test reached the pressure regulator delivery pressure earlier than it did for the Cycle 8 test, less protium was absorbed by the bed.

The difference in the absorption performance of the bed between Cycle 8 and Cycle 9 was noticed by the operator. Initially it was thought that protium supply tanks had leaked in air and that the air that did not react with the hydride was causing absorption blanketing.

Additional data for the Cycle 9 test are shown in Fig. 5. The bed was isolated from the protium supply tanks and the bed over-pressure evacuated. The bed was then re-connected to the protium supply tanks and the absorption test continued. The pressure regulator was bypassed to increase the absorption supply pressure, but this was still not adequate to achieve the desired bed loading. The bed was again isolated from the protium supply, evacuated, and then reconnected to the protium supply to finish the absorption test.

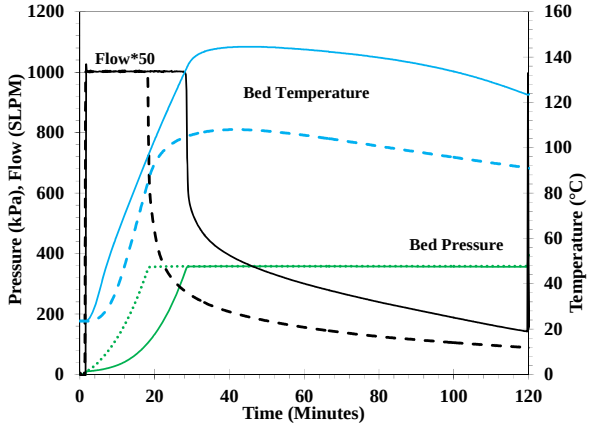

Fig. 4. SB-01 Absorption Cycle 8 (solid) and Cycle 9 (dashed) Results

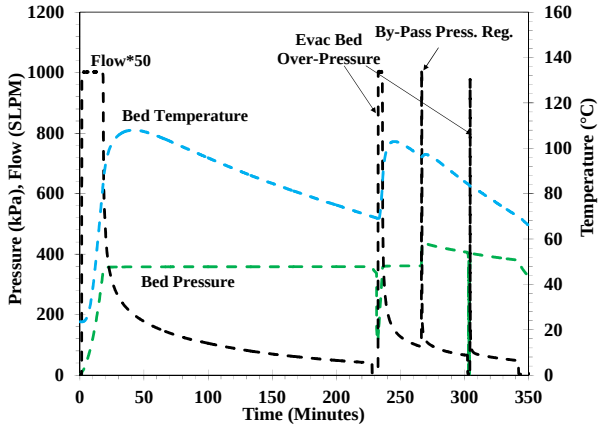

Fig. 5. Additional SB-01 Absorption Cycle 9 Results

V. DISCUSSION

It was discovered after the Cycle 9 test that the compressed gas cylinder of protium used to fill the test system tanks had been replaced with a full cylinder, but the cylinder was "Typical" Grade protium which has a minimum hydrogen purity of 99.95% (or less than 0.05% or 500 ppm) non-hydrogen isotopes. The maximum impurity levels stated by the vendor are 5 ppm oxygen, 400 ppm nitrogen, 10 ppm methane, 10 ppm carbon monoxide plus carbon dioxide, and 3.5 ppm water.

To examine the reduction in absorption rate in terms of inerts accumulating in the void space of the hydride bed, the follow were done using the absorption data for Cycle 8 and Cycle 9 with the results from Cycle 7 omitted to avoid clutter in the presentation of Cycle 8 results. Absorption enthalpy (ΔH) and entropy (ΔS) parameters were estimated from hydride pressure-composition-temperature (PCT) desorption data obtained at 30°C and 80°C: -47.28 kJ (-11.298 kcal) per mole H_2 and -123.70 J (-29.565 cal) per mole H_2 per K, respectively. These parameters were used to calculate bed hydride pressure using the measured bed temperature and plotted in Fig. 6 along with the measured bed pressure as a function of bed loading expressed in terms of hydrogen-to-metal ratio (H/M)

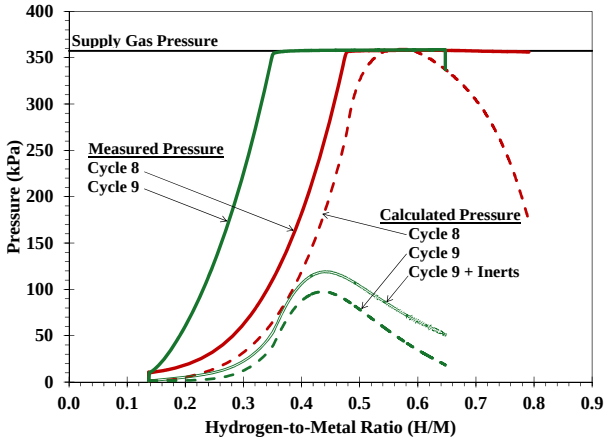

Fig. 6. Cycle 8 and 9 Pressures Versus Bed Loading

To calculate the contribution of inerts accumulated in the void space of the bed to the partial pressure in the bed for Cycle 9, it was assumed that 500 ppm of inerts were in the feed gas to the bed based on the vendor minimum protium purity. Using this impurity level in the bed protium supply as the inert gas mole fraction, the partial pressure of inerts in the bed void space was calculated using Eqn. 6 of Ref. [5] with the measured bed void volume of 1.896 L. The calculated inert gas partial pressure was added to the calculated hydride pressure for Cycle 9 and also plotted in Fig. 6.

The calculated Cycle 8 results shown in Fig. 6 are the anticipated results for an absorption test with a lag-time in measured temperature for using heater thermocouple values. As the bed absorbs protium, the temperature of the bed increases due to the energy released from the hydriding reaction and thus the calculated pressure of the bed. The increase in calculated bed pressure would produce a corresponding increase in the pressure at the inlet of the bed and this is demonstrated by the measured pressure data shown in Fig. 6. When the hydride pressure

approaches the protium supply pressure, the absorption rate and thus the rate of bed temperature increase decreases. Bed gas absorption continues based on the heat loss from the bed, but at a rate less than 20 SLPM.

The calculated Cycle 9 results shown in Fig. 6 are different than would be expected when using 500 ppm inerts in the feed gas system. The bed pressure as a function of protium absorbed would be expected to resemble the plot of calculated pressure plus inert partial pressure shown in Fig. 6 for Cycle 9 which is dramatically lower than the measured bed pressure.

Possible explanations for the deviation of the Cycle 9 absorption measured results from the calculated expected results are discussed. One possibility considered was the feed gas contained impurity levels higher than 500 ppm. Calculations were performed with various impurity levels in an attempt to create Cycle 9 calculated pressure plus inert partial pressure results similar in appearance to the Cycle 8 calculated results shown in Figure 6. It was determined using an impurity level of 5000 ppm (over 7 STP-L of inerts in the supply gas) was needed to reflect the appearance of the Cycle 8 results shown in Fig. 6 and thus this possibility dismissed. A similar change of a factor of 10 (smaller) in the void volume would produce results similar to using a 5000 ppm impurity level in the calculations.

Another possibility is that the impurities in the protium supply reacted with the hydride material and partially poisoned the hydride. Impurities in the supply gas which could react with the hydride include oxygen and carbon monoxide which is known to react with the LANA0.75 type hydrides.[8] If the hydride were poisoned with CO or another impurity, the removal of the over-pressure gas in the bed would not be expected to allow the hydride loading of the bed to continue as shown in Fig. 5 so this possibility was also dismissed. Similar comments can be made about oxidation of the hydride if oxygen were present in the supply gas (from air in-leakage) – the removal of the over-pressure would not be expected to allow the hydride bed loading to continue if oxidized.

It is assumed in all the calculations[3,4,5] that the gas phase composition, temperature, and pressure are uniform throughout the bed. These assumptions are not valid for large beds where there can be large temperature, pressure, and composition gradients throughout the bed. Concentration of inerts near or surrounding the hydride particles can readily explain the reduced hydriding rates even though the average bulk composition of inerts in the void space would be smaller.

VI. CONCLUSIONS

The presence of 500 ppm or less inerts can significantly impact hydrogen bed absorption rates. The impact on reducing absorption rates is significantly greater than predicted assuming uniform temperature, pressure, and compositions throughout the bed.

ACKNOWLEDGMENTS

The authors would like to thank Jody Dye for her contributions to this work. This manuscript has been authored by Savannah River Nuclear Solutions, LLC under contract No. DEAC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

REFERENCES

[1] "The Uranium-Tritium System – the Storage of Tritium." **Carlson, R.S.** [ed.] J.S., Wiffen, F.W. Watson. Gatlinburg, TN : Oak Ridge National Laboratory, *Radiation Effects and Tritium Technology for Fusion Reactors*. pp. 36-52. CONF-750989, Volume IV (1976).

[2] S. G. Smith, R. E. Johnson, and J. M. Miller, "Operational Problems with Uranium Pots Due to Helium Blanketing," *Fusion Technol.,* **28**, 1420 (1995).

[3] M. S. Ortman, T. J. Warren, and D. J. Smith, "Use of Metal Hydrides for Handling Tritium," *Fusion Technology.* **8,** 2330 **(**1985).

[4] S. Paek, D-H. Ahn, K-R. Kim, and H. Chung,, "Characteristics of Reactions Between Hydrogen Isotopes and Depleted Uranium," *J. Ind. and Eng. Chem.* **8**, 12 (2002).

[5] G. C. Staack and J. E. Klein, "The Effects of ^{3}He on Low Pressure Hydride Absorption Measurements with Tritium," *Fusion Sci. and Technol.*, **60**, 1479 (2011).

[6] E. G. Estochen and J. E. Klein, "Metal Hydride Wall Stress Measurements on a Four-Inch Short (FISH) Bed," *Fusion Sci. and Technol.*, **48**, 79 (2005).

[7] J. E. Klein and R. H. Hsu, "Air Passivation of Metal Hydride Beds for Waste Disposal," *Fusion Sci. and Technol.*, **54**, 79 (2008).

[8] F. G. Eisenberg, P. D. Goodell, "Cyclic Response of Reversible Hydriding Alloys in Hydrogen Containing Carbon Monoxide," J. Less-Common Metals, **89**, 55 (1983).