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HYDRIDE BEDS: ENGINEERING TESTS*

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ABSTRACT

The BNL Hydrogen Storage Program engineering effort is directed toward finding solutions to the engineering problems associated with metal hydrides--principally $FeTiH_x$. Measurements of thermal conductivity in non-enhanced, copper mesh-enhanced and aluminum foam-enhanced hydride beds have been made and indicate that the form of the enhancement material is the critical factor. The completion of the HYTACTS and its initial shakedown runs suggest the many applications for this new facility in the area of advanced hydrogen component testing. The performance testing of the Variable Parameter Test Unit-2 (VPTU-2) will begin following the BNL Safety Committee approval. A description of this vessel is included. The purpose, description and status of the Variable Parameter Test Unit -1 (VPTU-1) is reported as well as the results of the first set of tests performed in this vessel.

INTRODUCTION

The idea that hydrogen will be used on a large scale as an energy carrier in this country within fifty years is becoming fairly well accepted by at least the scientific community. The use of hydrogen presupposes the need for storage in a form that is safe, economically viable, and both environmentally and esthetically acceptable. Hydrogen, as well as most other gases, has traditionally been stored and transported as a compressed gas at pressures approaching 3000 psi in very heavy-walled steel cylinders. Hydrogen in liquid form, although orders of magnitude lighter in weight, is probably not a viable option because of safety and economic considerations.[1] Metal hydride storage is a proven technology which may have, because of their inherently high heats of reaction, greater application in the areas of chemical compressors and heat pumps, than in the hydrogen storage area.[2-4] Other occluder type materials such as molecular sieves have been considered in the past but were generally discounted due to their fairly low hydrogen storage density. Recently a small effort has been directed toward evaluating the viability of a new concept which involves the use of hollow glass microspheres for storing hydrogen.[5] Comparative energy storage densities can be found in Table I.

Although BNL has taken an active role in the evaluation of many hydrogen storage options, the "in-house" effort has been generally directed toward the development of the metal hydride storage concept. In the engineering area, where our efforts have focused primarily on iron-titanium hydride, solutions are being sought to the engineering problems presented by the characteristics inherent to this system. The fact that metal hydrides become extremely fragile, due to cracking upon hydrogen activation, causes the material to crumble into fine particles whenever the bed is disturbed. In larger systems (where the bed depth is greater than a "not-yet-determined" critical value) the forces generated by the expanding alloy as it absorbs the hydrogen are not only sufficient to greatly aggravate the attrition problem, but it has been reported that enough force can be generated to distort the walls of the pressure vessel.[6] As the hydrogen is made to flow through the hydride bed, fairly high pressure drops can also be experienced as the particles get very small after an extended number of charge/discharge cycles.[7] This will be an important consideration in fast-fluid flow-rate systems such as for automotive applications and for the chemical compressor application where even higher flow rates are anticipated. The poor thermal conductivity of the bed as a result of the many contact resistances is one of the problems on which BNL has applied its energies.

ENGINEERING TEST PROGRAM

Heat Transfer Enhancement

The addition of small amounts of high conductivity material to the hydride bed in an attempt to enhance the heat transfer was investigated. It was decided to use an approach that would involve the transient thermal transfer mode since the results would be more representative of actual operating conditions. The experimental apparatus included a thin-walled (2.45" I.D. x .095" wall) cylindrical copper vessel 11 1/4 inches long, rated at 200 psia, and flanged at both ends. Two temperature-controlled baths (30° and 30°C) were used to provide the constant temperature environment at the outside wall of the test vessel. Three shielded thermocouples were positioned at the vessel center line with longitudinal displacements of 2.3 inches between the hot junctions. The two extreme thermocouples were provided only to insure that end effects were minimal and heat flow was axial. All the data presented in this report were measured by the center thermocouple. For each set of experiments the test vessel was assembled, filled with hydride (2365 grams) and machine packed by raising and dropping the vessel with its holder (total weight 25 lb) a distance of 0.75 inches at the rate of 1 1/2 taps per second for 30 minutes (∿2700 taps). This procedure was adopted to eliminate variances in the bed's void fraction which was computed using bed height measurements taken through holes in the top flange. Each heating run was started by causing all three thermocouples in the test apparatus to approach the bath temperature (30°C) to within 0.2°C.

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The test vessel was then removed and immediately immersed in the high temperature (80°C) bath and the data measurement started. The rate at which the data were recorded was chosen so as to provide a minimum of fifty data points for each run. Generally each run was repeated three times and the results were extremely reproducible. Three configurations were used: 1) no enhancement, 2365 g packed bed of -30+50 mesh deactivated FeTi hydride; 2) the same bed with 5 wt % of the hydride removed and replaced with an equal weight of copper in the form of a knitted mesh;[9] 3) the same bed with 5.6% of aluminum in the form of a reticulated foam.[9] Each of these configurations was tested with 150 μm, 1.0 psia and 200 psia hydrogen pressure in the test vessel. The data were treated as given by Churchill, R.V., in his "Operational Mathematics."[10]

For the above geometry the solution of the temperature profile is given by:

$$\theta(\eta,\tau) = 1 - 2\sum_{n=1}^{\infty} \frac{J_0(\lambda_n\eta)}{\lambda_n J_1(\lambda_n)} e^{-\lambda_n^2\tau} \qquad (1)$$

where

θ = Dimensionless temperature at η and τ = $(T_W-T_0)/(T_t-T_0)$

η = Dimensionless radial distance from center = r/R

τ = Dimensionless time = $\alpha t/R^2$

α = Thermal diffusivity = $k/(\rho C_p)$ in ft^2/hr

k = Effective thermal conductivity of bed in $Btu/hr\text{-}ft^2\text{-}°F\text{-}ft$

ρ = Bulk density of bed = $\varepsilon\rho_g + (1-\varepsilon)\delta\rho_E + (1-\varepsilon)(1-\delta)\rho_H$

where g refers to gas, E refers to enhancement material and H to hydride.

C_p = Average specific heat of the bed = $\left[\varepsilon(\rho_g C_{pg}) + (1-\varepsilon)\delta(\rho_E C_{pE}) + (1-\varepsilon)(1-\delta)(\rho_H C_{pH})\right]/\rho$

ε = Bed void fraction

δ = Fraction of hydride replaced by enhancement material

λ_n = Bessel function value = 2.40483 for n=1

$J_n(\lambda_n)$ = Bessel function value = 0.51915 for n=1

T_W = Test vessel inside wall temperature (assumed to be the same as bath temperature)

T_0 = Bed center line temperature at t = 0

T_t = Bed center line temperature at time t

For sufficiently long times at the center line of the bed Eq. (1) indicates that

$$\ln\left[\frac{1}{1-\theta(0,\tau)}\right] = \lambda_1^2\tau - \ln\frac{2}{\lambda_1 J_1(\lambda_1)} \qquad (2)$$

Substituting $\alpha t/R^2$ for τ and the numerical equivalent for λ_1 and $J_1(\lambda_1)$ (2.40483 and 0.51915, respectively) into Eq. (2) and solving for α we get:

$$\alpha = \frac{\left[\ln\left[\frac{1}{1-\theta(0,\tau)}\right] + \ln\left[\frac{2}{\lambda_1 J_1(\lambda_1)}\right]\right]R^2}{\lambda_1^2 t} \qquad (3)$$

Solving Eq. (3) at the half time when T_t = 55°C we get:

$$\alpha = \frac{(.69315 + .47123)R^2}{5.7832\, t_{55}} = \frac{.002098}{t_{55}} = \frac{k}{\rho C_p}$$

The effective thermal conductivity can then be determined by measuring only the half time and calculating the bulk density and specific heat for each system tested.

$$k = \frac{.002098\rho C_p}{t_{55}}$$

The results are listed in Table II.

Four very definite conclusions may be drawn from these results:

- The greatest contribution to the thermal transport of the system is made by the hydrogen gas.
- The form of the enhancement material is a more important consideration than the conductivity of the material.
- The addition of 5.6% aluminum foam enhances the effective thermal conductivity of a hydride bed at 200 psi hydrogen by a factor of 2.6.
- This technique is a very convenient and quick method of screening new heat transfer enhancement concepts.

The thermal conductivity values for the no-enhancement runs compared favorably with measurements reported by Reilly[11] and Yu[12] being slightly higher than Reilly's but lower than Yu's. Both of their results were made using essentially the same bed material but an entirely different experimental technique.

Hydrogen Technology Advanced Component Test System HYTACTS

Since hydrogen technology is viewed as a long term but highly probable option, the establishment of a hydrogen test system where advanced component designs may be tested makes sense. Such a system has been completed at BNL and is undergoing the initial shakedown operation using nitrogen.

early Safety Committee approval, the HYTACTS will have completed testing on the Variable Parameter Test Unit-2 (VPTU-2) bulk hydrogen storage vessel by the end of the 1979 calendar year.

The HYTACTS is mainly a moderate pressure (600 psia) system that is constructed entirely of TIG welded, 316 stainless steel 1" schedule 10 pipe for the process gas, and 2" schedule 10 stainless steel pipe for the thermal transport system. Both the thermal transport fluid flow rate and the hydrogen flow rate are accurately controlled and measured by digital flow control valves (FCV). The FCV's are capable of maintaining constant fluid flow rates with changing upstream and downstream pressures and temperatures because of their built-in computer processor. The flow-rate range for the hydrogen valves (3) are from 20 SCFM to 6000 SCFM providing a wide operating range for a wide class of experimental apparatuses. The thermal transport system is closed and uses a 50/50 mixture of ethylene glycol and distilled water for heating and cooling. A 7.5 ton chiller and a 125 kW heater provide the cooling and heating at a fluid flow rate of 130 gpm for the assemblies under test. All test points are monitored by a Doric Digitrend 240 Data Scanner at the rate of 10 per second and each point may be dedicated to read one of five different functions and respond to any one of the four alarms on each. The data may be stored on either magnetic tape or floppy disc for analysis within the Tektronix 4051 Graphics computer. A compressor-purifier-dryer system not yet completed has the capability of upgrading tube trailer purity hydrogen (99.95%) to ultra pure hydrogen (99.999%) at the rate of 20 SCFM. With the puification system operational, off gas from test vessels can be purified, recompressed and stored in the 120,000 SCF volume storage tubes. The HYTACTS has been tested and is awaiting operating approval. All alarms and automatic shutdowns have been activated by simulated pressure or temperature excursions and the hygrometer and O_2 analyzer values are within acceptable limits. The first operation to be performed using the HYTACTS will be the initial activation of the alloy (3825 lb $TiFe_{.85}Mn_{.15}$) of the bulk storage vessel. This process will begin at the completion and acceptance by the BNL Safety Committee of the HYTACTS Safety Analysis Report.[13]

Variable Parameter Test Unit-2 (VPTU-2)

The VPTU-2 was built for the purpose of evaluating the fluidization concept of loosening a deep hydride bed and measuring the performance characteristics of a large vessel at various rates of constant hydrogen charge/discharge operation. The vessel was built by the Foster Wheeler Corporation under contract to BNL; and a detailed description and design considerations are included in their final report.[14]

Basically the vessel is a shell and tube heat exchanger that is flanged at one end for easy removal of the tube bundle. The vessel is constructed of A-106 Grade B pipeline steel, is rated for 500 psia working pressure and was proof-tested to 750 psia. The shell is 26" in diameter and has a torispherical head at each end. A number of 4" and 2" pipe nozzles provide access to the internals for gas, vacuum and water lines as well as feedthroughs for instrument lines. The vessel is 10 ft long overall with a 7-ft long hydride bed area. It contains 33 - 1" diameter stainless steel thermal transport "U" tubes, six fluidizing tubes at the bottom of the vessel and four filter vent tubes at the top. A spring--loaded hollow-center body 2" wide x 25" high runs the full length of the bed and acts as a crushable member to relieve the vessel wall of the expansion induced stresses.

A number of hydrogen charging/discharging cycles to the maximum storage capacity at times ranging from 5 hrs to 10 hrs will be completed. All pertinent bed temperature and pressure data will be recorded and the bulk storage vessel operating performance will be evaluated. A number of attempts will be made to confirm the viability of the fluidizing concept as a bed loosening technique. The rapid changes in pressure above and below the bed at incipient fluidization will provide the only data on which to base the assessment. The VPTU-2 is expected to perform according to the Foster Wheeler projections which are based on an empirical correlation of performance rate data from the 6"-ESEERCO/BNL vessel and the 12"--PSE&G/BNL vessel. The bulk storage vessel VPTU-2 will also be used to test the HYTACTS control systems and data acquisition.

Variable Parameter Test Unit-1 (VPTU-1)

This smaller vessel (24" O.D. x 3 ft long x 1/2" wall) was designed and fabricated at BNL for the purpose of screening new advanced concepts at a larger than bench scale but smaller than engineering scale. The shell, flange and end caps are all made of A-106-Grade B pipe line steel and it is rated and has been proof tested for a working pressure of 500 psia. Enough nozzles were provided for almost any internal configuration imaginable. A viewing port at the top enables viewing of the intervals with the aid of a fiberoptic boroscope. This feature was extremely valuable when attempting to evaluate the bed fluidization option. An 11" deep hydride bed was fluidized using nitrogen and helium and the results extrapolated to hydrogen to set the mass flow rate for the first fluidization attempt in the VPTU-2. The measured values were considerably higher than the handbook values using Leva's equation for minimum fluidization[15] probably because the bed was already well beyond the minimum fluidization point before we could visually detect motion. The VPTU-1 will next be used to determine the feasibility of using heat transfer panels, on which the thermal transport fluid channels are embossed, as the container for the hydride. The scheme, in actual practice, is to have the pressure vessel in the vertical orientation with conical heat transfer trays stacked in such a way that the top of one tray provides the heat transfer surface for the bottom of the tray above it. By limiting the tray depth, and consequently the bed depth, to less than some critical value (~4-6"), the hydride should be free to rise to the surface thus alleviating problems induced by the expanding hydride during the absorption of the hydrogen. A tray simulating a segment of a cone has been fabricated and installed in the VPTU-1 test vessel. The tray can be tilted by means of an external screw-jack mechanism in order to allow the hydride to slump toward one end of the tray thereby contacting the top heat transfer surface. Twelve thermocouples have been located in the bed to measure the temperature profile as a function of hydrogen flow rate and also as a function of tilt angle.

The system is ready for testing; but a re-emphasis of priorities has caused a hold in operation of test. No problems are anticipated but some doubt exists as to the adequacy of the heat transfer surface provided.

REFERENCES

1. Mathis, D.A., Hydrogen Technology for Energy, Noyes Data Corp., Park Ridge, New Jersey, (1976).

2. Powell, J.R., Salzano, F.J., Yu, W-S., and Milau, J.S. High Efficiency Power Cycles Using Metal Hydride Compressors, January 1975, BNL 50447.

3. Auh, P.C., Powell, J.R., Salzano, F.J., Beaufrere, A., and Fogelson, S.A. Design of Metal Hydride Compressor for 1000 MW(e) Central Power Plant, Final Report, October 1976, BNL 24076.

4. Lundin, C.E., Lynch, F.E., and Snape, E. The Development of Metal Hydride Systems for Hydrogen Compressor Applications, prepared for Jet Propulsion Laboratories under Consultant Agreement 686084, August 1978.

5. Taitel, R.J., Henderson, T.M., Luderer, J.E. and Powers, J. Microcavity Systems for Automotive Applications, Final Progress Report, prepared for Brookhaven National Laboratory under Contract 43615-S, November 1978.

6. Strickland, G., Milau, J., and Rosso, M. Some Observations on the Effects of the Volumetric Expansion of Iron-Titanium Hydride on Vessels Built at BNL, August 1977, BNL 23130.

7. Rosso, M.J., Strickland, G., and Milau, J.S. Pressure-Drop-Fluid-Flow Correlation For Fixed Beds of Small, Irregularly Shaped Particles, November 1976, BNL 50589.

8. Knitted copper mesh complimentary samples were provided by P.P. Usher, Metex Corp., Edison, N.J. The mesh was knitted of 0.0075" diameter wire triple crimped, Metex #R-76-5 1/2.

9. Aluminum foam manufactured by Energy Research and Generation, Inc., Oakland, California. 140 Grams of 10 pore per inch material with a measured density of 5.8% and 6.1% was added to the bed for a total aluminum density of 5.6%.

10. Private Communication from G.P. Delancy, Stevens Institute of Technology, Hoboken, New Jersey, and P.J. Fischer, Oak Ridge National Laboratory.

11. Reilly, J.J. and Wiswall, R.H., Jr., Hydrogen Storage and Production System II, August 1972 - June 1974, BNL 19436.

12. Yu, W-S., Suuberg, E., and Waide, C. Modeling studies of fixed-bed metal hydride storage systems, Proc. of THEME Conference, Miami, Florida, 1974.

13. Salzano, F., Strickland, G., Rosso, M., Bonner, M., and Schoener, G., Safety Analysis Report on the Hydrogen Technology Advanced Component Test System (HYTACTS) and Variable Parameter Test Unit-2, October 1979 (in press).

14. Franklin, H.N., Anelli, J., Kane, R., and Rabe, G., Use of Metal-Hydride Hydrogen Storage for Bulk Storage Applications, Final Report, prepared for Brookhaven National Laboratory, by Foster Wheeler Energy Corp., Livingston, N.J., July 1979.

15. Leva, M., Fluidization, p 63, McGraw Hill, New York, 1959.

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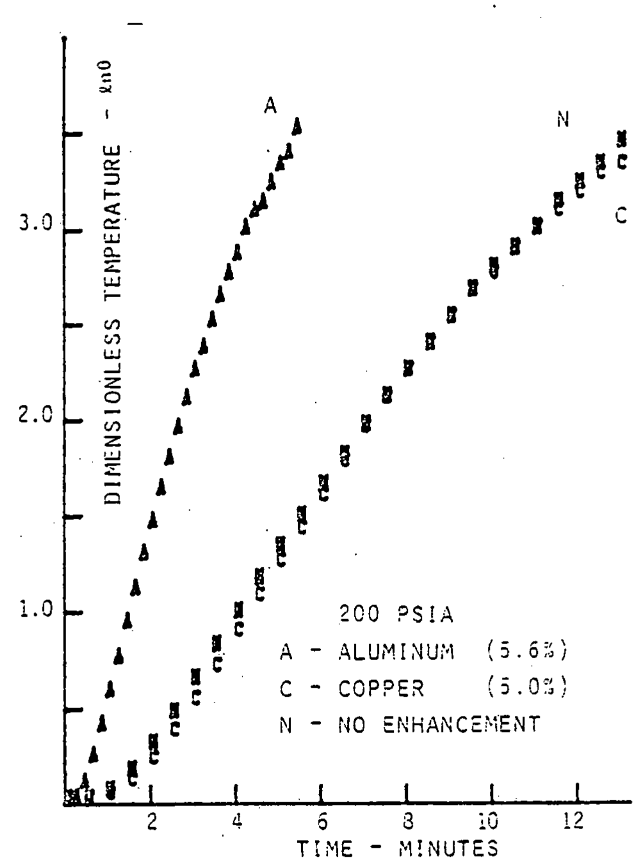

FIG. 1 RELATIVE MERIT OF THERMAL TRANSPORT ENHANCEMENT SCHEMES.

TABLE I

HYDROGEN STORAGE SYSTEMS PERFORMANCE/COST COMPARISON

	Compressed Hydrogen 2400 psi	MgH_x 10% Ni Hydride	FeTi Hydride	Micro-sphere	Liquid
*Gravimetric Energy Density Btu/lb	502 (1)	839 (1.7)	514 (1.4)	2390 (4.8)	7300 (14.5)
*Volumetric Density Btu/ft^3 x 10^3	32.4 (1)	61.1 (1.9)	59.8 (1.9)	50.6 (1.6)	113 (3.5)
Cost Dollars/MBtu	1.67	2.00	2.50	0.77	3.88

*Numbers in parentheses are normalized to compressed gas

TABLE II

HEAT TRANSFER ENHANCEMENT OF BEDS OF $FeTiH_x$

Run No.	Hydrogen Pressure	ε Void Fraction	Enhancement	α Thermal Diffusivity	k Effective Thermal Conductivity Btu/hr-ft^2-°F	$t_{.5}$ Half Time Minutes
3A	150 μm	0.490	None	0.000754	0.0189	167
1A-CE		0.497	5% Cu	0.00235	0.058	53.5
1G-AE		0.545	5.6% Al	0.00494	0.109	25.5
5A	1 psia	0.490	None	0.0148	0.371	8.5
2A-CE		0.497	5% Cu	0.159	0.394	7.9
2A-AE		0.545	5.6% Al	0.0829	1.834	1.52
8A	200 psia	0.513	None	0.0396	0.954	3.2
3A-CE		0.497	5% Cu	0.0362	0.902	3.5
3A-AE		0.545	5.6% Al	0.1122	2.497	1.12