DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program

Integrated Hydrogen Production, Purification and Compression System

Final Project Report

Linde LLC
Membrane Reactor Technologies Ltd.
Ergenics Corp.

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1.0 Executive Summary

1.1 Introduction

The project was started in April 2005 with the objective to meet the DOE target of delivered hydrogen of <\$1.50/gge, which was later revised by DOE to \$2-\$3/gge range for hydrogen to be competitive with gasoline as a fuel for vehicles. For small, on-site hydrogen plants being evaluated at the time for refueling stations (the “forecourt”), it was determined that capital cost is the main contributor to the high cost of delivered hydrogen.

The concept of this project was to reduce the cost by combining unit operations for the entire generation, purification, and compression system (refer to Figure 1). To accomplish this, the Fluid Bed Membrane Reactor (FBMR) developed by MRT was used. The FBMR has hydrogen selective, palladium-alloy membrane modules immersed in the reformer vessel, thereby directly producing high purity hydrogen in a single step. The continuous removal of pure hydrogen from the reformer pushes the equilibrium “forward”, thereby maximizing the productivity with an associated reduction in the cost of product hydrogen.

Additional gains were envisaged by the integration of the novel Metal Hydride Hydrogen Compressor (MHC) developed by Ergenics, which compresses hydrogen from 0.5 bar (7 psia) to 350 bar (5,076 psia) or higher in a single unit using thermal energy. Excess energy from the reformer provides up to 25% of the power used for driving the hydride compressor so that system integration improved efficiency. Hydrogen from the membrane reformer is of very high, fuel cell vehicle (FCV) quality (purity over 99.99%), eliminating the need for a separate purification step. The hydride compressor maintains hydrogen purity because it does not have dynamic seals or lubricating oil.

Figure 1 - The integrated hydrogen production, purification and compression system intends to reduce component count and costs while increasing efficiency

1.2 Approach

The project team set out to integrate the membrane reformer developed by MRT and the hydride compression system developed by Ergenics in a single package. This was expected to result in lower cost and higher efficiency compared to conventional hydrogen production technologies, as follows:

Lower cost compared to conventional fuel processors due to:

- Reduced component count and sub-system complexity
- Tight thermal integration of all reactions/processes in a single package
- Thermal metal hydride compression without rotating machinery, which should result in high reliability, low maintenance and low electricity usage

Higher efficiency resulting from:

- H₂ selective membranes within the reformer vessel to directly produce high-purity hydrogen, eliminating losses associated with a separate purifier
- Fluidized catalyst bed to improve heat and mass transfer
- Use of the compressor suction to lower the partial pressure of hydrogen in the reaction zone, which shifts equilibrium to enhance hydrogen production

- Thermal integration of the hydride compressor with the membrane reactor to reduce compression energy consumption

1.3 Objective, Tasks & Targets

The overall objective was to develop an integrated system to directly produce high pressure, high-purity hydrogen from a single unit, which can meet the DOE cost H₂ cost target of \$2 - \$3/gge when mass produced. The project was divided into two phases with the following tasks and corresponding milestones, targets and decision points.

Phase 1:

- **Task 1:** Verify feasibility of the concept, perform a detailed techno-economic analysis, and develop a test plan.
- **Task 2:** Build and experimentally test a Proof of Concept (POC) integrated membrane reformer / metal hydride compressor system.

Phase 2:

- **Task 3:** Build an Advanced Prototype (AP) system with modifications based on POC learning and demonstrate at a commercial site.
- **Task 4:** Complete final product design for mass manufacturing units capable of achieving DOE 2010 H₂ cost and performance targets.

Table 1 - Project Outline

	Key Task	Milestones	GO / NO GO Decision Points	Date
Phase 1	Task 1 Techno-economic assessment	Concept validated at lab scale	Feasibility of system integration confirmed	Feb-06
		Preliminary system design and economic model developed	Potential of achieving the cost target of \$2/kg H ₂ for a commercial system verified	
	Task 2 Proof Of Concept (POC) prototype	Unit commissioned with output capacity of 15 Nm ³ /hr, FC grade H ₂ at 100 bar	Integration of FBMR & MHC proven. System operability demonstrated	Jun-09
		Test data gathered and analyzed	Initial gas cost target of \$4.72/kg H ₂ at FBMR and MHC efficiencies of 71 and 69% respectively validated	
Phase 2	Task 3 Advanced Prototype	Unit commissioned with output capacity of 15 Nm ³ /hr or higher, FC grade H ₂ at 435 bar	System operability demonstrated; improvements over POC validated	TBD
		Test data gathered and analyzed	Intermediate gas cost target of \$2.81/kg H ₂ at DOE LHV efficiency validated	
	Task 4 Final system design for mass production	Commercial system designed and mass production concept defined	Feasibility of achieving final cost target of \$2/kg at 1500 kg/day and 500 units/yr scale demonstrated - Dec. 2009	TBD
		Final cost estimation and economics assessment completed		

1.4 Summary of Accomplishments & Status

Task 1 was completed as planned in Feb 06, which involved development of a conceptual system design and an economic model to demonstrate that the cost targets could be achieved as a result of the proposed system development. Task 1 also included assembly and testing of laboratory scale membrane reformer and hydride compressor units, which were operated together to verify the feasibility of the basic concept. A steady operation was achieved over the short test duration, and it demonstrated that the cyclic operation of the hydride compressor did not adversely affect the membrane reactor operation. A detailed report describing the findings and conclusions of Task 1 was issued earlier and is included in this report as an Appendix. Following is a summary of Task 1 accomplishments.

- Various reformer-membrane configuration options were studied and reformers with integral membranes with planar architecture were chosen since they offered high membrane area / catalyst volume, more compact reactors and ease of fabrication.
- Auto-thermal (ATR) and steam methane reforming (SMR) systems for different reactor geometries and 25 μm thick membranes were compared using modeling techniques and by conducting bench scale tests. Based on the results, ATR operation was selected.
- Different heat integration options for the Metal Hydride Compressor (MHC) and the fluidized bed membrane reactor systems were explored using process simulations.
- A detailed techno-economic analysis was completed.
- Experimental evaluation of a combined FBMR- MHC system was completed.
- Detailed design of integrated reformer / compressor components was completed.
- Efficiency versus capital cost calculation (within H2A and proprietary analysis tools) was completed.
- It was demonstrated that the target cost for this phase of the project of \$3.97/kg could be achieved.

With a GO decision from DOE based on the above, a plan was prepared for Task 2, which involved a detailed design of a Proof of Concept (POC) system, followed by construction, installation, commissioning and testing of the system.

Work on Task 2 began as planned in mid-2006, but completion was significantly delayed, first due to the delay in DOE funding in late 2006 and later due to serious financial issues with Ergenics, the developer of the hydride compressor system. The work on the membrane reactor development continued, and the POC unit with 15 Nm^3/hr H_2 capacity was fabricated, installed at the test site and commissioned in mid-2007. Preliminary testing of the reformer unit without the compressor began in late 2007, and continued through much of 2008. During this time eight runs of varying duration from 24 to 100 hours were conducted. In early runs, various mechanical issues were identified and resolved. However, one issue which persisted was lower hydrogen purity, attributed to membrane modules developing hydrogen leaks at various stages of operation. While the leakage issue was being investigated, runs were continued with partial loads of membrane modules.

In parallel, MRT continued to improve membrane integrity by modifying module fabrication procedures, performing extensive R&D efforts at bench scale and working with its membrane foil manufacturer to identify potential defects.

In early 2008, after almost a year delay, Ergenics resolved its financial issues and began work again to develop the planned hydride compressor unit. However, the progress was slow due to continued financial struggles. The redesigned compressor unit was completed in June 2008 and tested at the factory with pure hydrogen from cylinder supply. These tests confirmed the operability of the compressor under desired test conditions. However, during operation it was noticed that some of the hydride-filled tubes had developed leaks. Hence, work was continued in-house to resolve the issue.

In early 2009 the compressor unit with partial capacity was shipped to the test site in Vancouver, Canada, while efforts to resolve the leakage issues continued at the factory. In-house tests had confirmed that the unit with one less heat exchanger stage could compress greater than 15 Nm^3/hr H_2 from 7 psia to 200 psia. When design outlet pressure of 1,515 psia is desired, the flow capacity is reduced to 70% of the design value; nevertheless, the capability of desired compression ratio of 216 was confirmed. Thus, with all stages functioning, it can achieve the desired output flow and pressure simultaneously.

In March 2009, the membrane reactor and the hydride compressor were operated together as planned, albeit for a short duration, which confirmed the operability and capability of the combined system as per design and targets. The test results confirmed that the unit can deliver 15 Nm^3/hr H_2 at the desired purity when in full operation without leaks, and in conjunction with the metal hydride compressor. The following bullet points summarize Task 2 accomplishments:

- Over 1,000 cumulative hours of FBMR operation at 20 and 25 barg pressures
- Maximum production rate observed was 9 Nm^3/hr (based on modeling, projected to produce 15 Nm^3/hr with boost from MHC suction)

- Maximum methane conversion of over 60% achieved (over 85% conversion expected under design operating conditions)
- Axial temperature gradients observed to be less than 10°C
- Reactor Off-Gas (ROG) successfully routed to process burner to preheat reactor feeds (NG & air) and to generate steam
- Hydrogen output pressure of 100 bar achieved

Table 2. Summary of accomplishments against targets

Target	Status
15 Nm³/hr capacity (FBMR)	Maximum production rate of 9 Nm³/hr achieved, verifying design models. By extrapolating from models, full capacity is achievable with current design
15 Nm³/hr capacity (MHC)	Achieved with lower output pressure (leaking third stage heat exchanger bypassed)
100 bar output pressure	Achieved at lower flow rate (leaking third stage heat exchanger bypassed)
Product purity	Results have varied from 99.9% to >99.99%. Degradation due to abrasion from fluid bed not observed during >425 hour operation run
Continuous operation of > 400 hrs	Reformer system operated continuously for > 425 hrs
Unattended operation	Reformer operated unattended for one week. No operator actions required even during integrated run

During these tests, the main issues identified were reliability and durability of the system, primarily due to leaks gradually developing in both the reformer and compressor units. Other minor items observed related to better system integration to improve efficiency and overall performance. This was consistent with the plan to use learning from these tests to develop an improved design for the advanced prototype to be installed in the next phase of the project.

Although the proof of concept was accomplished, the leakage issues in both the units were seen as the major showstoppers in proceeding to the next step. It was therefore agreed with the DOE project managers to redirect the efforts with a focus on resolving the leakage issue before proceeding to Phase 2 of the project under a no-cost extension to the contract up until September 2010. A plan of action to resolve the leakage issue was prepared and followed. While significant progress was made with respect to improved manufacturing procedures for membrane modules (foil rolling and brazing), and alternative material of construction (copper vs. stainless steel) and improved soldering procedures for the hydride heat exchangers, the problems have not been fully resolved as yet. In light of extensive delays and lack of funding to continue the work, it was decided to end the project and report on the progress to date.

2.0 Task 1: Techno-Economic Analysis

The first task in this project was a detailed evaluation of the FBMR and MHC systems. Potential system configurations were developed, technically evaluated and down-selected for further analysis. Capital costs were estimated for systems of three different capacities (15, 100 and 670 Nm³/h) and a production volume of 200 units per year. Operational costs were calculated using H2A assumptions. A pilot scale FBMR-MHC system was assembled and tested to validate the concept as sound. The project team recommended the fabrication and testing of the proof-of-concept prototype (POC). Task 1 conclusions are presented below and the Task 1 report is included as “Appendix C - Task 1 Report” at the end of this report.

2.1 Task 1 Conclusions

A detailed assessment of the original project technical goals was conducted and a technology selection matrix was created for the different system generations. A systems integration study suggested that a fluidized bed membrane reformer system operating together with a hot gas heated MHC system is a technically viable option for the prototype POC system.

A study of the fluid bed membrane reactor system in two different operating modes, namely auto-thermal (ATR) and steam-methane reforming (SMR) with external heating, was conducted. Both were similar in cost and performance with the planned 25-micron membranes in the POC system. The future Advanced Prototype system with higher flux membranes favored the ATR system due to heat transfer engineering limitations in the SMR design. An experimental comparison of ATR vs. SMR reactor operation was also carried out using an MRT lab reactor. It was determined that adequate membrane flux values were realized for both modes of operation. However, the ATR system performance was somewhat better than the SMR system. Consequently, the ATR system was selected for further study.

Experimental validation of the proposed POC system integration scheme was completed using an MRT reformer and an Ergenics hot gas heated metal hydride compressor system. The main findings were:

- The 25 µm thick membranes, catalyst, and reactor conditions proposed for the POC validated the reactor design models. All subsequent design cases were based on this model. Hydrogen purities of 99.99+% were obtained for all tests.
- The fluid bed membrane reformer can be operated at steady state with sub-atmospheric hydrogen discharge supplied by a hot gas heated MHC.
- A metal hydride compressor using hot gas heating to vary bed temperatures between 30 and 450°C is feasible and it can compress hydrogen from 7 psia to >200+ psia (up to 1,900 psia) while maintaining a constant suction pressure.

Detailed engineering and capital cost analysis of the POC prototype system suggested that:

- When scaled to 1500 kg/day and by applying a discount factor for 200 units/yr, the POC prototype system cost is well within the project team’s initial technical goal of 4.72 \$/kg H₂.
- The economics of Advanced Prototype reactors with higher flux membranes are projected to improve as reactor costs drop with increasing flux. However, it is necessary to optimize sufficiently the balance of plant components since they constitute a large part of the total cost.
- Costs associated with palladium membrane (purchase or replacement) are a small percentage of the total system costs (reactor + compressor + BOP).
- The BOP encompasses a significant portion (37-55%) of the total costs and is needed to support the reactor architecture. Further optimization of this is important in order to approach the DOE goal, or to be competitive with commercial systems.
- Hydrogen compression accounts for about 18-27% of the total DMDL cost, which is expected because of the high compression ratio from sub-atmospheric pressure to 6500 psig.

Operational costs were calculated using the DOE H2A model and the following conclusions were drawn.

- A single POC unit producing 15 Nm³/hr H₂ at 1500 psig is technically viable. The estimated cost for delivered hydrogen with this first prototype unit is 10.84 \$/kg.

- Using the DOE H2A model approach, the estimated cost of hydrogen for a scaled-up version of the POC unit in volume production (1500 kg/day at 6500 psig, 200 units/yr) is \$3.97/kg.

The main risks and uncertainties associated with this project are as follows:

- The robustness and life of critical items, such as thin membranes, rotating equipment and high temperature switching valves, are untested at this stage. These could have long term reliability and O&M cost implications.
- Several prototype MHC units have been built but capacities as large as 15 Nm³/hr have never been attempted. The hot gas heating system, on which the hydrogen cost projections are based, also needs to be developed and tested.
- This unique approach for hydrogen production using an integrated system of two novel and untested technologies will require considerable operational experience before any further optimization or process improvements can be achieved.
- Further analysis of volume discount factors is required to reduce the uncertainty associated with the delivered hydrogen cost estimates.

2.2 GO / NO GO Decision

The Task 1 results were reviewed with the DOE Project Managers and a decision was made to GO forward to the next task of building a Proof of Concept (POC) unit with a capacity to produce 15 Nm³/hr H₂ at 99.99% purity and at 100 bar pressure.

3.0 Task 2: Assembly and Operation of the Proof of Concept Prototype (POC)

3.1 System Overview

A simplified flow diagram for the POC Integrated System is presented in Figure 2. The hydrogen production unit is MRT's FBMR, which operates as an auto-thermal reformer. Hydrogen produced within the reactor vessel passes through internal palladium alloy membranes and exits at very high purity. Ergenics' MHC absorbs the hydrogen at very low pressure and compresses it to 1,515 psia discharge pressure. Reactor off-gas (ROG) from the FBMR provides up to 25% of the energy required for compression, with the remainder provided by methane. Detailed flow diagrams, including for the POC and AP Systems are presented in Appendix A.

Figure 2 - POC Flow Diagram

The POC system was only partially integrated, as the FBMR and MHC were assembled as stand-alone skids that were interconnected in the field. By separating these two units, experimentation could be performed with each unit independently, so the performance of each could be fully understood before operating them together. This approach resulted in several redundant components, such as a separate burner that produces hot water for the MHC and a separate control cabinet, to enable stand-alone testing. This redundancy would be eliminated in the Advanced Prototype; the FBMR vaporizer would supply hot water to the MHC and a single system would control both units.

3.2 Detailed Design of the POC

3.2.1 FBMR System

The key components of the FBMR system are the membranes, reactor vessel and vaporizer. The remaining components are largely off-the-shelf pumps, compressors, heat exchangers, valves, etc.

3.2.2 Membranes

The FBMR system uses rectangular hydrogen diffusion membrane panels. A panel is comprised of two palladium alloy foils that are bonded to each side of a porous metallic substrate. The substrate is fused within a 6" x 11" stainless steel frame using a proprietary method developed by MRT (refer to Figure 3). 25 μm thick palladium foils were used for the POC membrane panels.

Hydrogen diffuses atomically through the solid metal membrane. Sievert's Law, shown below, describes the hydrogen flux across Pd alloy membranes of the type used in this project.

Equation 1: $N = J \cdot A / \Delta X \cdot (\sqrt{P_{H_2,r}} - \sqrt{P_{H_2,p}})$, where:

N = hydrogen flux (mol/s m^2)

J = permeability ($\text{mol/m s } \sqrt{\text{Pa}}$)

A = membrane area (m^2)

ΔX = membrane thickness (m)

$P_{\text{H}_2,\text{r}}$ = partial pressure of hydrogen on retentate side (Pa)

$P_{\text{H}_2,\text{p}}$ = partial pressure of hydrogen on permeate side (Pa)

The permeability (J) of the membrane is a function of the metal composition and temperature. Pd membrane permeability increases with temperature, but membrane stability puts an upper operating limit of about 600°C .

As illustrated in Figure 4, for a membrane operating at a given temperature, the flux is proportional to the difference in the square root of the hydrogen partial pressures across the membrane. An effective method to increase the hydrogen flux across the membrane is to reduce the partial pressure of hydrogen on the permeate side. In lab scale settings, this is typically accomplished by introducing diluents to the permeate stream, such as nitrogen or steam. In the case of the POC system, a pure hydrogen product is desired, so the absolute permeate pressure must be lowered to reduce the hydrogen partial pressure. This is achieved through the use of the MHC, which creates a sub-atmospheric suction pressure (vacuum) with minimal energy impact.

Membrane integrity is of utmost importance to maintain high hydrogen purity. Membrane panels are first tested for leak integrity during the palladium alloy foil bonding procedure. After panels are installed into the POC reactor, a cold leak test is performed. During this test the reactor is pressurized to 25 barg with nitrogen at ambient temperature. Each membrane outlet is then connected to an open water container and the number of escaping nitrogen gas bubbles is counted. This count is then used to calculate an estimated leak rate which can be correlated to an expected product purity during the run. During the run, product purity is measured directly using a gas chromatograph. After the shutdown a second cold leak test is performed.

3.2.2.1 Reactor Vessel

The reactor vessel incorporates a dual compartment design which creates a thermal boundary enabling the use of low cost metals for fabrication. Within this boundary, membranes are exposed to a precious metal catalyst bed fluidizing at 550°C and 25 barg. Although the FBMR operates at temperatures as high as 550°C , the dual compartment design allows the use of carbon steel for fabrication of the outer shell, reducing the overall reactor cost by as much as 25%.

Cartridge heaters are installed inside the reaction zone to provide heat for startup. Once the reactor reaches reforming temperatures, air is introduced in addition to steam and methane to maintain the heat

of reaction, resulting in a directly heated auto-thermal reactor. Traditional reformers are indirectly heated by having high temperature flue gases flow across the outside of the reactor walls. This method of heating becomes economically unpractical in smaller reformers used for forecourt refueling because it requires relatively large heat transfer surface areas fabricated from expensive metals that can withstand elevated surface temperatures. A novel method of air introduction to the reformer minimizes syngas dilution in the membrane zone, thus maintaining a high H_2 flux.

Easy access to membrane panels was identified as a key design requirement for maintenance. As shown in Figure 5, five membrane panels are mounted onto a rectangular flange to form a membrane module, which is inserted through an opening on the side of the FBMR vessel. The vessel has five openings to accommodate the full complement of 25 membrane panels. Each membrane module can be individually accessed, without having to move or open the entire FBMR vessel.

Figure 5 - Novel auto-thermal Fluidized Bed Membrane Reactor (FBMR) enables use of lower cost metals, while better membrane access eases maintenance.

3.2.2.2 Vaporizer

The FBMR includes a novel vaporizer developed by MRT (Figure 6). Within this single unit, reactor off-gas (ROG) is combusted and used to preheat, vaporize, and superheat a natural gas and water mixture. A forced air burner with two fuel ports is located at the top of the vaporizer. One port accepts natural gas for start-up and the other accepts ROG, which reduces natural gas duty during continuous operation. The high temperature flue gas travels across heat exchanger tube coils installed within an annulus around the combustion chamber. The heat exchanger tube coils are fed with a natural gas/water mixture for preheating prior to entering the FBMR vessel. The detailed design of the vaporizer included the use of computational fluid dynamics (CFD) modeling to optimize heat transfer. Results from a CFD study are illustrated in Figure 7.

Figure 6 - MRT's novel vaporizer increases efficiency by burning ROG.

Figure 7 - During vaporizer development, computational fluid dynamics modeling was used to optimize heat transfer.

3.2.3 POC-specific Design Modifications

A number of design changes were made to the FBMR system to reduce complexities associated with the operation of new equipment.

3.2.3.1 Compartmentalization of the skid

In the Task 1 design, a compartmental design approach was taken to separate areas with flammable services requiring a higher electrical classification zone. This separation would enable the use of general rated equipment for non flammable services, reducing balance of plant costs. To increase access to skid components during testing, this compartment concept was not used for the POC design in order to allow more layout flexibility.

Figure 8 - FBMR system on-site at National Resources Canada, Institute for Fuel Cell Innovation.

Figure 9 - FBMR balance-of-plant components include a water pump and air blower (left), low cost compact heat exchangers (center) and control & safety valve rack (right).

3.2.3.2 Natural Gas Delivery

A three-stage, oil-less compressor was proposed to deliver natural gas (NG) to the reformer at 377 psia in the Task 1 design. An HDS system using a slip stream from the product hydrogen was proposed to capture naturally occurring and odor-additive sulfur from the source NG supply. To utilize existing equipment whose operation was known and proven, this method of NG pretreatment and delivery was replaced by two “off the shelf” NG vehicle refueling compressors, which had a much higher discharge pressure (3000 psig) than required for the reformer, but were less expensive and simpler to operate at the POC capacity. A conventional absorbent-based sulfur capture system operating at ambient temperature was installed downstream of the compressors.

The capacity of these commercial compressors is approximately 65% of the required POC capacity. Two compressors were installed in parallel with a buffer tank. Designed to nominally compress NG to 3000 psig, the compressors were routed to a DOT stamped 65L compressed gas cylinder. This NG delivery system was operated in batch mode with a low pressure switch installed on the cylinder to trigger an automatic start request to the compressors. An internal compressor high pressure switch triggered a shutdown once the cylinder reached full pressure. A water-jacketed regulator was used to step down the NG pressure to the reformer skid to compensate for the Joule-Thompson cooling effect.

Two existing 25 L vessels were filled with a zeolite based sorbent and installed upstream of the NG compressors to capture sulfur from the gas supply.

3.2.4 Metal Hydride Compressor (MHC)

Information about compressing hydrogen with metal hydride alloys is presented in “Appendix B - Metal Hydride Hydrogen Compression.” A simplified flow diagram for the MHC is shown in Figure 10.

The MHC uses three stages to compress hydrogen from 7 psia to 1515 psia for a net compression ratio of 216. It consists of two metal hydride beds that are alternately heated and cooled using a 50:50 mixture of non-toxic propylene glycol and water. Each bed contains 3 hydride heat exchangers, one for each stage. The beds measure 6 inches in diameter by 36 inches long. The MHC is assembled on a skid measuring 6 ft. long by 5 ft. deep by 8 ft. high. The skid contains a natural gas-fired hot liquid heater, a fan cooler that rejects heat to ambient air, and the associated piping, valves and controls.

Figure 10 - MHC Simplified Flow Diagram.
Check valves prevent hydrogen backflow

As originally proposed, the MHC was to be heated with a hot liquid ($\sim 140^{\circ}\text{C}$) produced using waste heat from the FBMR, supplemented with a natural gas fired heater. During the Task 1 Techno-Economic Analysis design effort, Ergenics proposed the MHC be powered by hot gas in lieu of hot liquid. Hot gas could provide much higher temperature ($\sim 450^{\circ}\text{C}$) which would increase MHC operating efficiency and reduce its size. However, during the detailed design phase, Ergenics was not able to source large diameter gas valves capable of sealing the 450°C circulating gas stream. As a result of these issues, Ergenics elected to return to the hot liquid heated design when the project was resumed.

Figure 11 - The two MHC hydride beds are small and compact.

Figure 12 - The MHC (foreground) is adjacent to the FMBR skid.

This view shows the control panel, fan cooler (lower left) and NG/ROG fired hot liquid heater (lower right).

The MHC hydride beds contain Ergenics' patented ring manifold miniature hydride heat exchangers. Hydride alloy is retained within 1/16" dia. tubes. Twenty four tubes are spirally wound around and connected to a central hub, forming the ring manifold. Hydrogen enters and exits each tube through the central hub. This modular design lends itself to low cost assembly, using mass production techniques.

Ring manifolds are stacked together to form very high surface area heat exchangers.

Heat exchangers are placed within an internally insulated liquid jacket (or shell), to reduce sensible heat loss.

For the POC MHC, each shell contains three heat exchangers, one for each stage. The first stage is comprised of 30 ring manifolds which contain a low pressure hydride alloy capable of absorbing hydrogen at sub-atmospheric pressure to maintain a high hydrogen flux through the FBMR membranes. The second and third stages are comprised of 23 ring manifolds each and they contain progressively higher pressure hydride alloys, resulting in an overall compression ratio of 216.

The two shells measure 6 inches in diameter by 36 inches long. In operation, one is heated with hot liquid (50:50 mixture of propylene glycol & water) while the other is cooled with ambient temperature liquid. The hot and cool liquid streams are alternated between the shells every 50 seconds, compressing hydrogen from 0.5 bara to 100 bara (7 psia to 1,515 psia).

Figure 13 - Modular Ring Manifolds are the building blocks for Miniature Hydride Heat Exchangers

4.0 Experimental Results

The FBMR system was completed in the summer of 2007 and was started up and operated in a number of campaigns without the MHC. In March of 2009, the MHC was delivered to the site and connected to the FBMR. The systems were run together a few times before their respective leakage issues led to the redirection of the effort.

4.1 FBMR System Alone

Assembly of the reformer skid was completed in the summer of 2007 and the skid was installed at the NRC Institute for Fuel Cell Innovation (IFCI) site in Vancouver, Canada. Between the summer of 2007 and the spring of 2008, eight reformer test campaigns were conducted with varying membrane loads. Over 400 hours of reforming test time was achieved during these initial runs.

Since membrane panels are expensive and time consuming to make, only 3 or 4 panels were installed for the first four test runs to avoid potential damage associated with start-up unknowns. During these commissioning trials, balance of plant mechanical deficiencies were identified and addressed.

4.1.1 October 2007 Week-long run

A full membrane compliment was installed for a week long campaign in October, 2007. During the startup of this run, a significant number of impurity breakthroughs were observed across the membranes. After a post run investigation, it was determined that an internal reactor heater had fractured during a startup process upset. The fractured heater debris remained in the fluid bed during operation and caused mechanical damage to the surface of several membranes.

The heater electrical configuration was modified to prevent future heater fracture and the reactor was loaded with 12 out of 25 membrane panels.

4.1.2 December 2007 Week-long run

A week long run was conducted in December, 2007. During this run operation of the reformer skid was stable with a temperature profile of less than 10°C across the reforming bed. Product purity was consistent during the run; however, increased membrane leak rates were observed after shutdown.

An investigation revealed that the leak had most likely developed due to foil deformation associated with Pd hydrogenation/dehydrogenation and differential coefficients of expansion between the foil and the porous metal substrate. Shut down procedures were revised to minimize the deformation in the membrane by controlling hydrogen partial pressures. In addition, thermal stresses were reduced by controlling cooling rates during reactor shutdown.

A brief run was conducted in April, 2008 with a membrane compliment of 10 panels to gauge the effect of revised shutdown procedures. Unfortunately, this run was halted prematurely due to a failure of the reactor air distributor. A new air distributor was fabricated and installed after the run and the reactor was prepped for a full membrane load run.

4.1.3 July 2008 Week-long run

The FBMR system was successfully operated continuously over the period from July 6th to July 11th, 2008. The objectives of this run were to gather performance data with a full load of membrane panels, validate process models, reduce NG thermal duty requirements with reactor off-gas, and to determine additional actions required, if any, to move to unattended operation.

The system operated for over 65 hours at reforming temperatures above 500°C. Initial data was gathered at a reactor pressure of 20 barg for a period of 36 hours. After operation was shown to be stable, the reactor pressure was increased to the design value of 25 barg for the final 30 hours of testing.

During the run, a hydrogen production rate of 9 Nm³/hr was achieved, corresponding to a methane conversion of greater than 60%. These values are consistent with model predictions for the operating conditions. Axial temperature profiles along the membrane bed were within an average of 10°C. Electric startup heaters were used to supplement heat losses associated with the small size of the system.

The use of reactor off gas as a secondary burner fuel to preheat the process feeds was successfully demonstrated.

Figure 14 - Hydrogen production and average bed temperature - July 2008

Figure 15 - Hydrogen production and reactor pressure - July 2008

Post run membrane leak testing showed 11 panels out of 25 experienced an increase in leak rate, revealing that the revised shut down procedure was only partially successful in eliminating leak formation. Based on further tests in conjunction with National Resource Canada Institute of Fuel Cell Innovation (NRC-IFCI) and discussions with the membrane foil supplier, inconsistency in foil quality appeared to be the primary reason for membrane degradation.

Supplier feedback indicated that the machine used to fabricate the 6 inch wide POC foils did not maintain consistent quality. A smaller machine was capable of maintaining desired quality in a 4.72 inch wide foil. New panels were fabricated with the narrower foils. This reduced overall membrane area in the reactor, but production rates could be easily extrapolated to prove performance. Fifteen 4.72 inch panels were fabricated.

4.2 MHC Alone

The MHC was completed in June, 2008 in anticipation of the July, 2008 campaign. During factory testing at Ergenics, leakage was observed in the ring manifold heat exchangers. The unit was kept at the factory pending resolution of the leakage.

The leaks occurred through the tube walls and in solder joints where the tubes were attached to the central manifold. Efforts to resolve the leak issue were partially successful.

Many new ring manifold heat exchangers were fabricated in the second half of 2008, but with the problem only partially resolved (repairs restored 5 of the 6 hydride heat exchangers). In order to prevent further delays, the MHC was completed without one of its stage 3 heat exchangers.

In this condition, the MHC achieved >250 L/m (the design flow rate) with two stages of compression (7 psia in, 200 psia out and 70% of the design flow rate at the design outlet pressure of 1515 psia (CR=216). These results confirm that the MHC would be able to satisfy the performance requirements for flow rate and outlet pressure if both stage 3 heat exchangers were present.

The MHC was not operated long enough to accurately measure isothermal efficiency.

The MHC was delivered to the site in February, 2009 and was interconnected with the FBMR.

Minor shipping damage was repaired and the data acquisition system was replaced due to a memory problem. The unit was started and operated alone on bottled hydrogen on two separate days before the integrated campaign.

Figure 16 - Through-wall tube leaks occurred in small diameter tubing

Figure 17 - The MHC maintained sub-atmospheric suction pressure to increase FBMR hydrogen flux (less than 0.5 bara (7 psia) shown here) and discharged hydrogen at >105 bara (1,515 psia)

4.3 Integrated POC Testing

4.3.1 FBMR Reformer

In preparation for the integrated runs, a full membrane compliment was installed. Out of the 25 membrane panels, 10 were with the larger foil size (6" x 11") and 15 were the new 4.72 inch size. Three of the narrow panels were blocked off prior to the run, due to high cold leak rates believed caused by physical damage during transportation and/or installation of the modules. The installed membrane area represented 78% of the design capacity.

4.3.2 FBMR-MHC Operation

The FBMR skid was started on March 16, 2009 for an integrated campaign and was operated for a period of greater than 425 hours, including one week of unattended operation. Initially, a production rate of over 7 Nm³/hr and methane conversion of greater than 60% was observed. These results corresponded with process model predictions for the smaller effective membrane area and the absence of suction from the compressor.

The FBMR was operated at 20 barg and 550°C for a period of 24 hours to observe base line performance before starting up the MHC.

As shown in Figure 18, the FBMR and MHC operated well together. The upper chart in Figure 18 shows MHC performance when field tested using bottled hydrogen alone. When connected to the FBMR, suction pressure was maintained below atmospheric. As shown in Figure 19, hydrogen flow rate increased as predicted during MHC operation.

Figure 18 - Integrated FBMR-MHC operation was stable

During integrated operation, float vents on the MHC water system actuated periodically, indicating the continued presence of hydride heat exchanger tube leaks. After several hours of operation, the MHC was turned off to prevent further hydrogen leakage.

After the MHC was shutdown, production from the FBMR was found to be steadily decreasing (refer to Figure 19). It was determined that this decline in production was not related to the MHC operation. Also, the decline had not been observed in previous runs. Gas chromatograph analysis of the reformer exhaust gas showed a decrease in methane conversion following the drop in production. This drop in conversion and production lasted for approximately 75 hours and reached a stable value. The new value was significantly lower than thermodynamically predicted values, even without the additional forward boost from membranes. It was determined that deactivation of the catalyst was the likely cause.

Figure 19 - Hydrogen production decreased during the March 2009 run.

During the run, the product impurity flow rate was calculated by comparing the product purity (analyzed with a gas chromatograph) with the hydrogen product flow rate, resulting in an average total leak rate of 21.7 ml/min. As illustrated in Figure 20, it was found that the product impurity flow rate remained relatively constant during the campaign, indicating no new membrane pinholes had been formed. By extrapolating with a full production value of 15 Nm³/hr, a product purity of greater than 99.99% can be expected, corresponding with pre-run cold testing (see Figure 21).

Figure 20 - Hydrogen purity remained high during the 400+ hour campaign.

Figure 21 - Hydrogen will be >99.99% pure at the full flow rate.

As in prior runs, post run tests showed an increase in membrane leak rate.

Post run catalyst analysis confirmed that performance degradation was due to sulfur poisoning. Membrane hydrogen flux did not appear to be affected by the sulfur breakthrough.

4.4 Results Summary

Accomplishments with respect to targets set during Task 1 are listed below.

4.4.1 15 Nm³/hr Capacity (FMBR)

A production rate of 9 Nm³/hr was achieved during the full membrane compliment run of July, 2008, without the boost from partial vacuum on the permeate side with the use of the MHC. This production rate agrees with the value predicted from process design models and extrapolation of model results shows that full capacity is achievable with the current design.

4.4.2 15 Nm³/hr Capacity (MHC) and 100 Bar Output

MHC performance measured with one of the third stage hydride heat exchanger bypassed is consistent with meeting this target if the bypassed bed was present. See paragraph 4.2 above.

4.4.3 Product Purity

Results have varied from 99.9% to > 99.99% product hydrogen purity after resolving mechanical deficiencies. An important observation during the experimental trials was the absence of membrane degradation during steady state operation. This observation suggests that there are no adverse effects on membrane modules due to abrasion from the fluid bed during runs at least as long as 425 hours.

4.4.4 Stability of continuous operation

The reformer system was operated continuously for over 425 hours during the spring of 2009. The system was unattended for one week during this run. Even during the integrated portion of this run with the MHC, no operator interventions were required.

4.5 Issues

Two technical issues were identified during experimental testing: reduced product purity after the shutdown transition stage and continuing hydride heat exchanger tube leaks. As a result of continuing problems, we proposed to redirect the project towards the resolution of the following issues via a one year no-cost extension.

4.5.1 Reduced Product Purity

During early trials of the reformer, various balance of plant mechanical deficiencies resulted in membrane panel damage during runs. Upon rectifying these deficiencies, the project team observed consistent purity results during steady state conditions. This answered a major technical unknown regarding the

impact of abrasion from the fluid bed on membranes. Post shut down testing found that membranes had developed pinhole defects during the shutdown stage that would result in lower product purity. Subsequent lab testing found that a significant factor contributing to the formation of these defects was the presence of trace hydrogen in the reactor at lower temperatures. Shutdown procedures were revised to improve reactor purging which resulted in an improvement but did not fully eliminate the occurrence.

Discussions with membrane foil suppliers led to the decision to use narrower membrane foils fabricated on a smaller rolling machine. Upon physical inspection, these narrow foils were observed to have a higher quality than that of the larger foils. Results from the spring 2009 campaign also showed that membrane modules made with these new, narrower foils had lower increases in leak rates after shutdown.

The use of better quality foils has resulted in more stable membrane panels. Better manufacturing consistency is required across the membrane manufacturing cycle from the production of membrane foils to the bonding process.

4.5.2 Hydride heat exchanger tube leaks

It was discovered that during operation small diameter, thin-walled tubing develops pin-hole leaks. Ergenics is working with suppliers to identify causes and cures. Until problems with thin-walled tubes are resolved, Ergenics is specifying thicker walled tubes which have not developed leaks.

5.0 Redirect Effort To Resolve Issues

5.1 *Reduced Product Purity*

Two double-sided membrane panels were fabricated with 3"x12" frames, one with 25 μm Pd-25% Ag alloy foil and one with 15 μm foil. Both foils were manufactured using the supplier's new rolling machine. The physical appearance of these foils was better than that of previously obtained foils.

The two membrane panels were put inside a vessel with separate permeation outlets. For a majority of the testing, the panels were exposed to a hydrogen-helium mixture and periodically exposed to pure helium for leak measurements. Leak rates were measured using a bubble flow meter, flux was measured using a thermal mass flow meter, and permeate composition was measured using a gas chromatograph.

Figure 22 shows a comparison of hydrogen permeation flux measured for the new 25 μm membrane at 550°C with data obtained from a membrane panel fabricated from a 25 μm Pd-25% Ag alloy foil manufactured by the Vendor's old rolling machine. Similarly, results for the new 15 μm membrane are shown in Figure 23. Within the experimental error, all permeation fluxes are consistent.

After varying temperatures from 450 to 550°C and pressures from 3 to 26 bar for 2,045 hours (see detailed conditions in Figure 24), permeation flux was measured for both membrane panels using pure hydrogen. Due to equipment limitations, testing at 550°C and 26 bar was not possible. Upper limits were set at 550°C at 20 bar and 26 bar at 450°C. The results are given in Figure 25 with a comparison to the initial permeation rates. As shown in Figure 25, no significant decrease in permeability was observed during 2,045 hours of testing.

As seen in Figure 24, the 25 μm Pd-Ag alloy foil panel developed leaks at 550°C and 20 bar but remained very stable under other test conditions. The effect of temperature appears to be greater for the 15 μm Pd-Ag foil than that of the 25 μm Pd-Ag foil. The 15 μm foil did not develop new pinholes at 450°C and 26 bar but developed pinholes at 500°C and 550°C, even when pressures across the membrane were low. This sensitivity to temperature is illustrated in Figure 26. At 500°C and 2 bar, leaks across the 15 μm Pd-Ag foil increased with time at 500°C and 2 bar. In contrast, the 25 μm foil remained relatively stable.

Based on He leak tests, if the membrane modules are run in the reformer at 550°C and 20 bar, a hydrogen purity of ~99.99% for the 25 μm Pd-Ag foil and ~99% for the 15 μm Pd-Ag foil can be expected.

MRT is continuing to study the leak mechanism and improve fabrication techniques. We are also working with our foil supplier to improve foil quality through the reduction of impurities and defects. Testing conducted during the re-direct effort suggests that operating at 550°C and 25 barg exceeds the optimal operating envelope for our current Pd-Ag membranes. In order to achieve consistent high-purity hydrogen, we may need to operate the reformer at cooler temperatures (design 550°C) or at lower pressures (design 25 barg), which would result in requiring slightly higher membrane area in the FBMR. Continued membrane testing is required to define the boundaries of this optimal operating envelope for membranes with improved foil quality and fabrication techniques.

Figure 22 - Hydrogen permeation flux of 25 μm Pd-25% Ag foils as a function of partial pressure driving force at 550°C

Figure 23 - Hydrogen permeation flux of 15 μm Pd-25% Ag foils as a function of partial pressure driving force at 550°C

Figure 24 - Helium leak of the membrane panels vs. testing time under various conditions

Figure 25 - Hydrogen permeation flux of the membrane panels as a function of partial pressure driving force at 550°C at hour 1 and 2045 of testing.

Figure 26 - Helium leak rates in the membrane panels at 550°C and 2 bar.

5.2 Hydride heat exchanger tube leaks

To date, the solder joint leaks have been eliminated, but the cause of the through-wall leaks has not been fully identified or resolved. Leaks have occurred in both welded and seamless drawn tubing with different degrees of annealing and different materials, including stainless steel and copper.

Ergenics is working with several tubing suppliers to try to resolve the leakage issue. Small diameter tubing, whether seamless or welded, is drawn from larger diameter tubing. Many factors affect the quality of the drawing process, including material composition, hardness and die quality. One supplier of stainless steel welded and drawn tubing performed eddy current testing in an effort to assure the tube walls were defect-free. These tubes would not leak water when hydro-tested to several thousand psi, but would not reliably contain hydrogen.

Currently, ring manifolds fabricated with thicker-walled tubing appear to be more robust (0.01" vs. 0.006") and testing continues to determine whether the problem is solved.

6.0 Economics

6.1 Introduction

Economics for the Integrated Hydrogen Production, Purification and Compression system were initially analyzed in Task 1, with results presented in the Task 1 report (refer to Appendix). Capital cost was calculated for a single small system and scaling factors for system processing capacity and volume production were applied, using methods presented in “Techno-Economic Prospects of Membrane Reactors in a Future Hydrogen Driven Transportation Sector”.¹ The Task 1 analysis used assumptions for energy costs, production capacity and volume from the H2A Hydrogen Production Modeling tool (beta version), but the H2A model itself was not employed.

The project team first used the updated version of the H2A modeling tool in November of 2007 to reflect lessons learned during the POC design effort and figures were updated in June, 2009 after the integrated system was operated in the field.

6.2 Approach

The target DOE forecourt hydrogen production rate is 1,500 kg/day, with an intermediate production goal of 100 kg/day. The POC prototype was rated to produce 32.4 kg/day of hydrogen. For greater accuracy in its cost estimates, the project team elected to fully analyze the integrated system on the 100 kg/day capacity before extrapolating economic predictions for the much larger 1,500 kg/day system.

Variables for a 100 kg/day “base case” using POC parameters were input into the H2A spreadsheet. Then, the effect of potential improvements for several key parameters was determined, before scaling the results up to the 1,500 kg/day design capacity.

6.2.1 Key parameters identified during POC operations

The project team identified that system economics and, ultimately, the H2A predicted cost for hydrogen delivered by the integrated system are primarily affected by MHC isothermal efficiency and Membrane Robustness. MHC isothermal efficiency translates directly into NG feedstock consumption, while Membrane Robustness involves capital cost and replacement frequency and costs.

6.2.1.1 MHC Isothermal Efficiency

The MHC employs the Carnot thermodynamic cycle. Carnot cycle efficiency is a function of the temperature difference between the energy source and the heat rejection sink. The MHC currently operates with a hot liquid temperature of 140°C and an ambient air heat rejection temperature of 40°C, corresponding to Carnot efficiency of 22.4%. The degree to which the MHC can approach Carnot efficiency depends on minimizing thermal losses, primarily those associated with sensible heat. The MHC employs Ergenics’ sensible heat recovery technique to increase isothermal operating efficiency. The sensitivity analysis looked at MHC efficiencies of 16% (66% of Carnot), 19% and 22% (~90% of Carnot), with the base case using 16%.

6.2.1.2 Membrane Life

The base case assumes the FBMR membrane modules will need annual replacement. As factors related to maintaining membrane integrity are improved, the replacement interval can be extended. The effect of 3 and 5 year replacement frequencies was evaluated.

6.2.1.3 Membrane Thickness

Membranes are comprised of Pd-Ag alloy foils. Reducing membrane thickness increases hydrogen flux (see Figure 3 on page 8) and reduces material cost. The POC employed membranes of 25 µm thickness, so the base case includes 25 micron membrane costs. MRT is also developing membrane modules with 15 micron thick foils and their impact on cost reduction was evaluated.

¹ “Techno-Economic Prospects of Membrane Reactors in a Future Hydrogen Driven Transportation Sector”, by M. Sjardin, K.J. Damen, and A.P.C. Faaij. Utrecht University, 3584 CS Utrecht, The Netherlands (2005).

6.3 Base Case

The H2A results for the Base Case are presented in Table 3. Base Case variables include 16% MHC isothermal efficiency, 25 micron thick membranes and 1 year membrane life (annual replacement). The Base Case includes costs associated with producing only a single unit.

Table 3 - Economic Analysis Base Case

Base Case System – Production Volume of One		
Parameters	H2 Production	100 kg/day
	MHC Thermal Efficiency	16%
	Membrane Life	1 year
	Membrane Thickness	25 microns
H2 Production Cost Contributions (\$/kg H2)	Capital	8.39
	Fixed O&M	1.81
	Feed Stock	2.09
	Other Utilities	0.06
	Total H2 Production Cost	\$12.35/kg
Compression, Storage, and Dispensing Cost Contributions (\$/kg H2)	Capital	1.35
	Fixed O&M	1.74
	Other Utilities	0
	Total C.S.D. Cost	\$3.08/kg
Total H2 Cost		\$15.43/kg
System Efficiency (LHV)		50.4%

6.4 Parametric Sensitivity Analysis

The reduction in hydrogen cost associated with potential parameter improvements are presented in Figure 27, Figure 28 and Figure 29. The parameters judged most likely to be achieved are circled and subsequently used in the sensitivity summary presented in Figure 30.

Figure 27 - Hydrogen Cost Sensitivity to MHC Thermal Efficiency

Figure 28 - Hydrogen Cost Sensitivity to Membrane Life

Figure 29 - Hydrogen Price Sensitivity to Membrane Thickness

Figure 30 - Sensitivity Analysis Identifies 30% Reduction in Hydrogen Price

6.5 Increasing Production Volume

Anticipated reductions in hydrogen cost resulting from manufacturing multiple systems per year is tabulated in Figure 31. Methods defined in “Techno-Economic Prospects of Membrane Reactors in a Future Hydrogen Driven Transportation Sector”¹ were employed. The annual volume initially specified by the DOE in its 2003 Program Plan was 200 units, and that number was used in this analysis. The specified annual production rate was subsequently increased to 500 units, but the project team preferred to not take credit for savings that might result from the additional volume.

Figure 31 - Volume Production Reduces Hydrogen Cost by 43%

6.6 Scaling Up from 100 kg/day to 1,500 kg/day

In similar fashion to predicting cost reductions associated with volume production, the final step was to calculate costs associated with the full-sized forecourt hydrogen production system. As shown in Table 4, the results are compared with the DOE "standard model", as well as to costs reported by competing leading firm at the time, H2Gen. The integrated system hydrogen production cost is calculated to be 5% lower than the DOE standard model and 9% lower than the H2Gen system.

Table 4 - The Integrated System Can Deliver Hydrogen at the Lowest Cost

		100 kg/day Integrated System ¹	1500 kg/day Integrated System ¹	1500 kg/day H2A Standard ²	1500 kg/day H2Gen Projected ³
H2 Production Costs (\$/kg H2)	Capital	2.13	0.80	0.45	
	Fixed O&M	0.72	0.18	0.16	
	Feed Stock	1.99	1.99	0.91	
	Other Utilities	0.06	0.01	0.10	
	Production Cost	\$4.90/kg	\$2.97/kg	\$1.61/kg	\$2.70/kg
Comp, Stor, & Disp Costs (\$/kg H2)	Capital	1.35	0.10	1.26	
	Fixed O&M	1.74	0.23	0.46	
	Other Utilities	0	0	0.16	
	C.S.D. Cost	\$3.08/kg	\$0.33/kg	\$1.88/kg	\$0.94/kg
Total H2 Cost		\$7.98/kg	\$3.30/kg	\$3.50/kg	\$3.64/kg

1. Integrated system parameters: 15 micron, 3 year life membranes, 19% MHC efficiency, 200 units/year

2. DOE H2A Standard, 500 units/yr.

3. H2Gen presentation to 2009 DOE Program Review Meeting, 500 units/yr.

7.0 Appendix A

The following two pages contain:

7.1 *Process Flow Diagram for 15 Nm³/h POC System*

7.2 *Process Flow Diagram for 15 Nm³/h AP System, used for H2A economic analysis*

8.0 Appendix B - Metal Hydride Hydrogen Compression

Reversible metal hydride alloys are intermetallic compounds that absorb hydrogen. When this happens, hydrogen is distributed compactly throughout the metal lattice. The key to practical use of metal hydrides is their ability to both absorb and release the same quantity of hydrogen more than a million times without deterioration.

In chemical shorthand, a typical reaction can be expressed as:

where M represents the metal and H is hydrogen.

The reaction is reversible and its direction is determined by the pressure of the hydrogen gas. If the pressure is above a certain level (the equilibrium pressure), the reaction proceeds to the right to form a metal hydride; if below the equilibrium pressure, hydrogen is liberated and the metal returns to its original state. The equilibrium pressure, itself, depends upon temperature; it increases with increasing temperature and vice versa.

The hydrogen sorbing behavior of metal hydride alloys is characterized using equilibrium pressure-temperature-composition (PTC) data. This data is determined by keeping an alloy sample at constant temperature while precisely measuring the quantity of hydrogen sorbed and the pressure at which sorption occurs. The quantity of hydrogen sorbed is expressed in terms of alloy composition, either as an atomic ratio of hydrogen atoms to the number of atoms in the base metal alloy, or as the capacity of hydrogen in the alloy on a weight percent basis.

As shown in Figure 32, most of the hydrogen is absorbed in a region where there is little pressure change. This region of near-constant pressure is known as the plateau pressure. Metal hydride formation is also accompanied by hysteresis, which appears as the difference between the upper absorption curve and the lower desorption curve in Figure 32.

The plateau pressure moves up with an increase in temperature and down with a temperature decrease. Figure 33 shows several PTC plots for the same alloy at several different temperatures and illustrates the basis of hydride-based compression. Low pressure hydrogen is absorbed into an alloy at low temperature. Once it is full of hydrogen, the alloy is heated to release its hydrogen at elevated pressure.

Figure 33 illustrates that a modest temperature increase results in a substantial pressure increase. The pressure rise associated with increasing temperature in the plateau region is exponential; a temperature rise of only 75 C (from 25 to 100) results in a ten-fold pressure increase from ≈ 0.4 atmospheres to greater than 5 atmospheres. (The theoretical pressure increase is 12.5, however, inefficiencies in nature, such as heat transfer resistance and hydrogen pressure drop, tend to reduce the increase in actual practice.)

Figure 32 - Pressure-Temperature-Composition Absorption and Desorption Isotherms for Ergenics' Hy-Stor® 207 alloy at 25°C.

When filled to capacity, Hy-Stor 207 alloy ($LaNi_{4.7}Al_{0.3}$) holds 1 hydrogen atom for each metal atom to become $LaNi_{4.7}Al_{0.3}H_6$ when fully hydrided.

Figure 33 - PCT Isotherms illustrate how the energy in heat increases pressure.

Hydride alloys can be engineered to operate at different temperatures and pressures by modifying alloy composition and production techniques. By employing successively higher pressure hydride alloy stages in series, high pressure ratios can be generated. For example, a 3 stage hydride compressor will compress a 7 psia inlet pressure to 1,515 psia, resulting in a compression ratio of 216 (refer to Figure 34).

Continuous high pressure hydrogen flow is produced by providing two identical hydride heat exchanger "beds" and utilizing simple and reliable one-way hydrogen check valves between each hydride stage (refer to **Figure 35**). When one of the hydride beds is heated and the other bed is cooled, hydrogen absorption and compression occurs simultaneously. After hydrogen transfer is completed (in about 50

seconds), the hot and cold liquid flow is reversed and hydrogen absorption and compression, again, occurs simultaneously. The use of one-way hydrogen check valves prevents the hydrogen from back flowing, thus, simply and passively allowing the hydrogen to flow into the next higher pressure hydride stage whenever a small pressure differential of about 1 psi is present.

Figure 34 - Multi-stage hydride compressors achieve high pressure using energy in hot liquid.

Figure 35 - Continuous hydrogen compression is accomplished with two identical hydride heat exchanger beds operating 180° out of phase.

9.0 Appendix C - Task 1 Report