

# **ADVANCED THERMAL HYDROGEN COMPRESSION**

**Mark Golben  
David H. DaCosta  
Ergenics, Inc.  
247 Margaret King Avenue  
Ringwood, NJ 07456**

## **Abstract**

Ergenics, Inc. is developing a novel thermal hydrogen compressor that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression and hydrogen utilization process. The thermal compressor is an absorption-based system that uses the properties of reversible metal hydride alloys to silently and cleanly compress hydrogen; hydrogen is absorbed into an alloy bed at ambient temperature and, subsequently, is released at elevated pressure when the bed is heated with hot water. Compression energy can be supplied by waste heat or solar hot water. Two recent innovations strongly suggest that thermal compressors can be used for non-pure hydrogen streams likely to result from advanced production methods. The first involves a combination of processes that permit the absorption of impure hydrogen streams by hydride alloys. It may be possible to employ these processes to remove contaminants that may damage fuel cells or advanced storage materials located downstream from the compressor. The second innovation is a modular alloy bed design that permits rapid hydrogen absorption kinetics, enabling a reduction in compressor size with an associated reduction in capital cost. The results of an investigation into the feasibility of integrating purification processes with thermal compression is presented in this paper, along with engineering design considerations for miniature modular hydride heat exchangers. Preliminary data from thermal compressor tests at 5,000 psig outlet pressure are included.

## Introduction

Ergenics is investigating the application of its novel thermal hydrogen compression process to hydrogen produced from renewable resources. Thermal hydrogen compressors have offered significant operational and economic advantages over traditional mechanical compressors when the hydrogen is pure and flow rates are relatively low. However, hydrogen produced from renewable resources can contain impurities that might damage a thermal compressor and, if thermal compressors are to play a major role as hydrogen becomes an increasingly important part of America's energy supply, increased flow rate capabilities must be economical. In addition, new storage systems require hydrogen pressures of 5,000 to 10,000 psig, much higher than the current industrial practice of 3,600 psig.

The thermal compressor is an absorption-based system that uses reversible metal hydride alloys to silently and cleanly increase hydrogen pressure. Previously, reversible metal hydride alloys would sustain damage from hydrogen impurities at low levels of <50 ppm. Ergenics has developed three processes that may permit hydride alloy beds to tolerate higher levels of impurities, in some cases up to 10,000 ppm or more. Passive Purification is used for water vapor and oxygen, Elevated Temperature Desorption is used for CO and CO<sub>2</sub>, and Automatic Venting can clear inert gas blanketing caused by N<sub>2</sub> and CH<sub>4</sub>. Employing these processes in a thermal compressor may assure long operational life.

A secondary benefit could be realized if the purification processes would not only protect the compressor from contaminant-caused damage, but also remove contaminants that damage or degrade performance of downstream equipment. For example, carbon monoxide can damage electrode catalyst in PEM fuel cells. Combining compression with purification can potentially increase fuel cell performance and extend fuel cell electrode life. There is even the potential to use compression with purification to resolve system-level issues that may be encountered with new, high energy density hydrogen storage materials currently under development. Some of these new materials must be charged at elevated pressure and may be sensitive to impurities.

In work reported last year (DaCosta 2000), Ergenics accomplished the following tasks:

- we classified the hydrogen composition and operating conditions expected to result from various advanced production techniques to determine which processes would be good candidates for thermal compression;
- we identified the three techniques that can mitigate the effect that impurities have on thermal compressor operation; and
- we prepared a preliminary design for a 3,600 psig, 2,000 scfh refueling station thermal compressor, compared the thermal compressor with a mechanical compressor and performed a hazardous operation analysis.

Subsequent investigation focused on using a thermal compressor to provide the dual function of compression and purification to mitigate fuel cell degradation from CO. We developed a correlation for CO removal that can be used to optimize hydrogen compressor/fuel cell systems.

Thermal hydrogen compressors have been limited to applications with relatively low flow rates (<400 scfh) due to heat transfer limitations associated with large alloy beds. In order to permit economical scale-up to production-sized units competitively superior to mechanical compressors, Ergenics has developed and patented an advanced hydride bed design with rapid heat transfer capabilities. The hydride bed is essentially a miniature high surface area hydride heat exchanger, which permits the construction of large compressors of small size and cost. The small hydride beds can be thermally cycled at a rapid rate ( $\approx 2$  minutes) in order to process high hydrogen flow rates. The unique hydride heat exchanger design is modular and lends itself to high-volume, low-cost production.

The emerging need to compress hydrogen beyond the current industrial practice of 3,600 psig provides additional incentive to develop thermal compression, in order to obviate increased maintenance associated with mechanical compressors operating at such high pressures. Alloy development and tests to verify the ability of hydride alloys to function in the 5,000 psia range and beyond have commenced.

## **Thermal Compressor Purification Processes**

### **Impurity Effects on Hydride Alloys**

Gaseous impurities expected to appear in hydrogen produced from renewable resources include the “usual subjects” - water vapor, air (including oxygen, nitrogen, and argon), carbon monoxide, carbon dioxide, and methane (DaCosta 2000). Impurities interact with hydride alloys with varying effects (Sandrock 1984), as follows:

- *Poisoning* results in a rapid decrease in hydrogen capacity with cycling. Damage from poisoning tends to be localized on the alloy particle surface, so it is often possible to restore performance with little, if any, loss in capacity. Oxygen and CO are impurities that poison alloys.
- *Retardation* is manifested by a reduction in absorption kinetics without loss in ultimate capacity. With enough time, full capacity can be achieved. Retardation is often a result of impure species forming weak bonds on the alloy surface that impede hydrogen absorption. Carbon monoxide and water vapor retard hydriding.
- *Reaction* causes irreversible capacity loss through bulk corrosion of the alloy. Reaction results in the formation of very stable chemical compositions that do not reversibly hydride and cannot be easily returned to their original state. Active sulfur compounds such as SO<sub>2</sub> cause irreversible damage due to the reaction mechanism.
- *Innocuous Blanketing* results from impure gas species congregating on the alloy surface and forming a blanket that reduces the rate of hydrogen absorption. Gases that cause blanketing, such as nitrogen and methane, are easily removed by venting.

### **Purification Processes for Use With a Thermal Compressor**

Ergenics has developed three processes, summarized in Table 1, that permit hydride alloy beds to tolerate higher levels of impurities.

**Table 1. Thermal Compressor Purification Processes**

| <b>Impurity</b>                      | <b>Process</b>                  | <b>Comments</b>  |
|--------------------------------------|---------------------------------|--|
| H <sub>2</sub> O, O <sub>2</sub>     | Passive Purification            | Hydride Heat Exchanger in-situ process prevents retardation and poisoning. Removes O <sub>2</sub> from hydrogen. |
| CO, CO <sub>2</sub>                  | Elevated Temperature Desorption | 115°C desorption removes CO impurities from alloy surface.   |
| N <sub>2</sub> , Ar, CH <sub>4</sub> | Automatic Venting               | Clears inert gas blanketing and removes impurity from hydrogen.  |

### ***Water Vapor and Oxygen***

Water vapor is the most common contaminant in hydrogen. It affects hydride alloys through the mechanisms of retardation followed by poisoning. When hydrogen absorption begins, water vapor is carried towards the alloy surface by the hydrogen. The water molecules gather and become concentrated on the alloy surface, slowing the passage of hydrogen to the alloy (retardation).

Hydride alloys contain nickel, which normally acts as a dissociation catalyst for hydrogen molecules prior to absorption. The nickel can also act as a weak catalyst for dissociating water molecules. As water molecules are dissociated at the surface of the alloy particles, the resulting hydrogen would be absorbed into the alloy, but oxygen tends to react with the rare earth element (lanthanum or mischmetal), forming a stable oxide that is no longer available to hold hydrogen. Hydrogen absorption capacity decreases (poisoning).

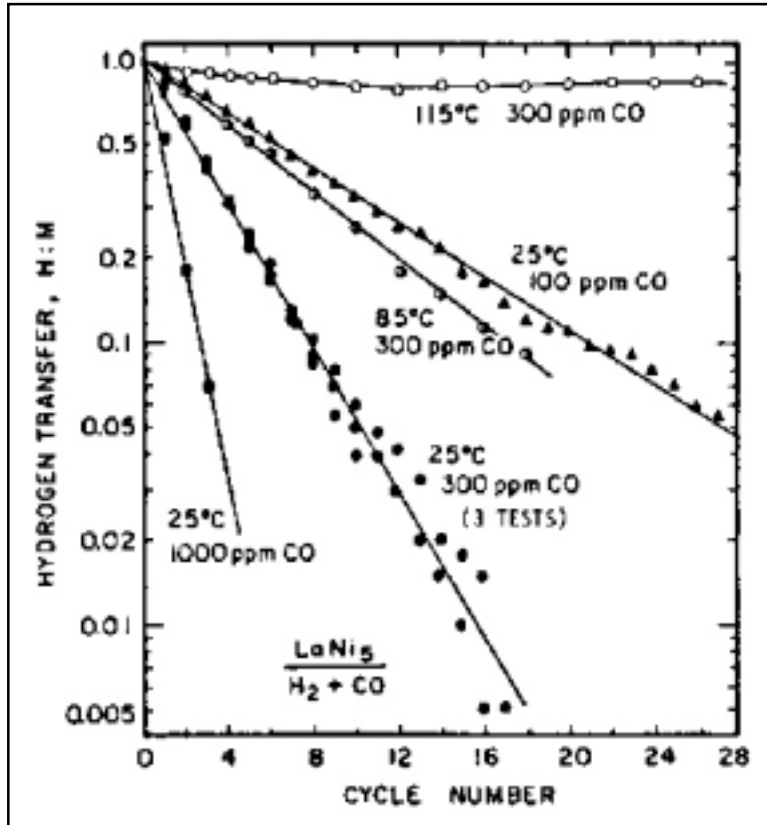
Nickel-metal hydride battery alloy development by Ergenics and others stimulated a large body of research into the corrosion of hydride electrodes immersed in electrolytes. A number of corrosion inhibiting additives, such as cobalt and tin, have been identified for immersed alloys, and we have found these to have positive impact on preventing poisoning in gaseous systems as well.

Ergenics has developed a method of removing water vapor and oxygen from hydrogen within a hydride alloy bed (Golben 1999). This in situ purification process permits the alloy to operate as if it was absorbing clean, dry hydrogen. Named "Passive Purification," the process includes catalytic recombination of oxygen impurities, physical water removal and the use of corrosion inhibitors in the alloy formulation. During desorption of dry hydrogen from the alloy, water that was removed during the absorption process is evaporated into the hydrogen as it exits the bed. The Passive Purification process successfully permits cycling hydride alloys with hydrogen that is saturated with water vapor and contains some oxygen.

### ***Carbon Monoxide and Carbon Dioxide***

It has been suggested that a single monolayer of CO and, to a lesser degree, CO<sub>2</sub> prevents hydrogen absorption into hydride alloys, probably by forming Ni-carbonyl bonds on the alloy surface that deactivate the dissociative properties of the nickel (Sandrock 1997). Figure 1 shows the effect of cycling LaNi<sub>5</sub> alloy in hydrogen contaminated with CO. Interestingly, there is

almost no degradation of performance cycling at a temperature of 115°C. This suggests that an elevated temperature desorption can remove the CO molecule from the alloy to restore full performance. More importantly, the CO can be vented during this desorption process and removed from the hydrogen stream. CO removal may prolong the life of catalysts used in fuel cells or other downstream equipment.



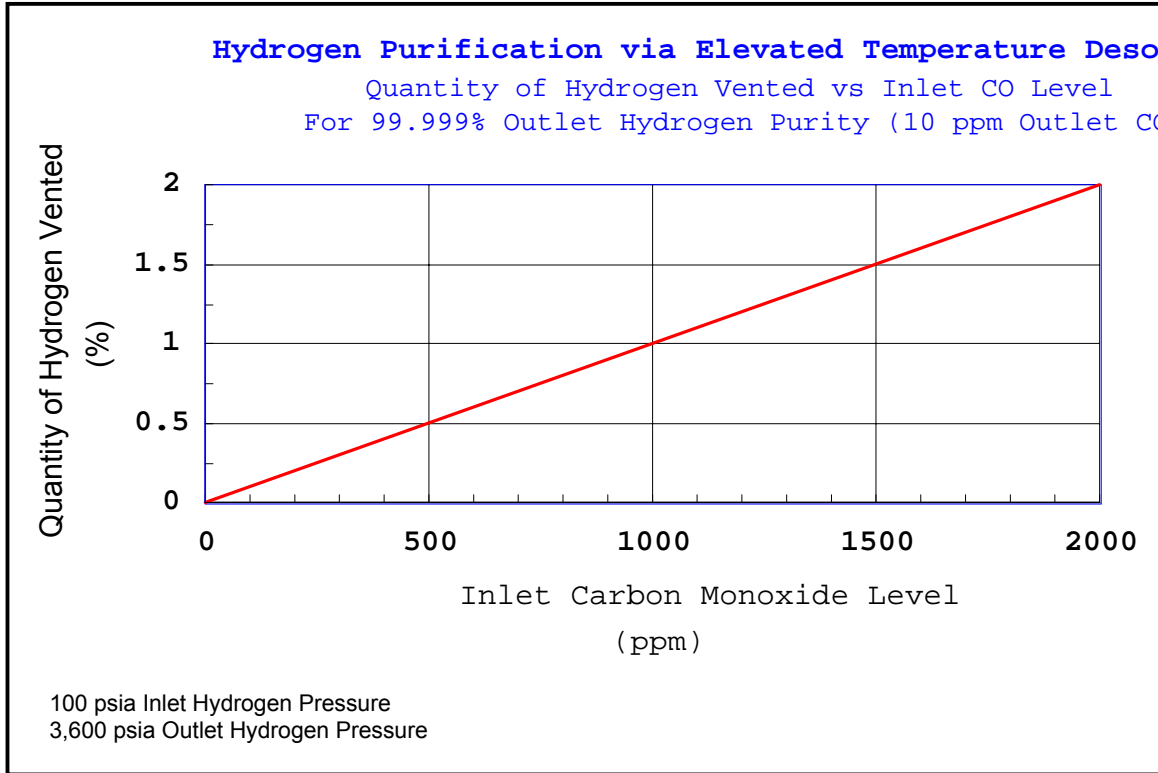
**Figure 1:** Elevated temperature desorption removes CO from LaNi<sub>5</sub> hydride alloy. (Eisenberg 1983)

When CO is vented, the hydrogen required to sweep it away will be lost. Ergenics has calculated a relationship between the CO inlet concentration, the CO outlet concentration and the quantity of hydrogen that will be vented in the process. A curve that shows this relationship for an outlet hydrogen purity of 99.999% (10 ppm CO) appears in Figure 2. From this data, it will be possible to predict optimal conditions for a compressor/fuel cell system. The thermal compressor venting process can be fine-tuned to remove enough CO to prolong fuel cell catalyst life, but prevent excessive venting of hydrogen fuel.

### ***Nitrogen and Methane***

Nitrogen, methane, noble gases, and ammonia do not react with hydride alloys, but if present in enough quantity, can form an innocuous blanket, that reduces the rate of the hydrogen absorption to a crawl. During a desorption cycle, hydrogen can be used to sweep away impurities that cause innocuous blanketing. In a similar fashion to elevated temperature desorption suggested for CO

removal, these gases can be either removed from the hydrogen stream by an automatic venting process or be allowed to pass through the compressor.



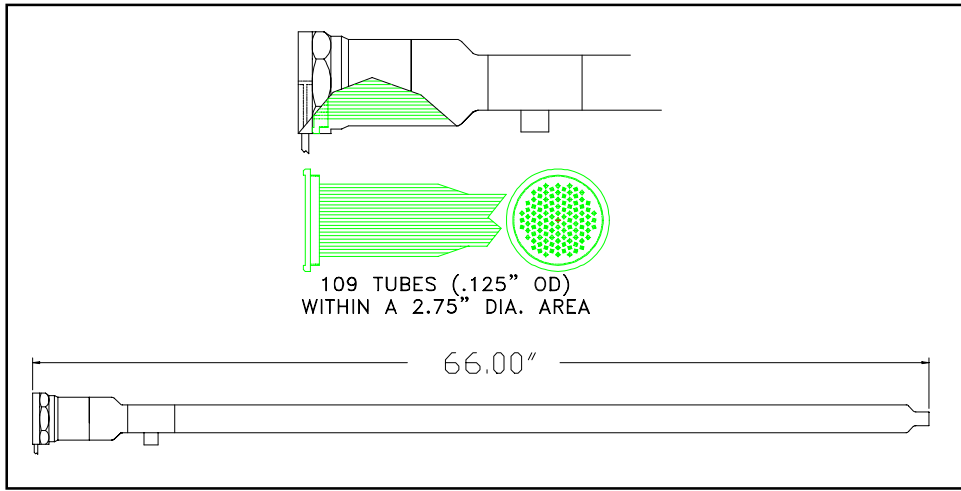
**Figure 2:** Thermal compressors can remove CO from hydrogen to protect fuel cell catalyst.

### Miniature Modular Hydride Heat Exchangers

In order to process the higher flow rates of hydrogen expected from advanced production processes, Ergenics has developed and patented an advanced hydride bed design with rapid heat transfer capabilities. The hydride bed is essentially a miniature high surface area hydride heat exchanger, which permits the construction of large compressors of small size and cost. The small hydride beds can be thermally cycled at a rapid rate ( $\approx 2$  minutes) in order to process high hydrogen flow rates.

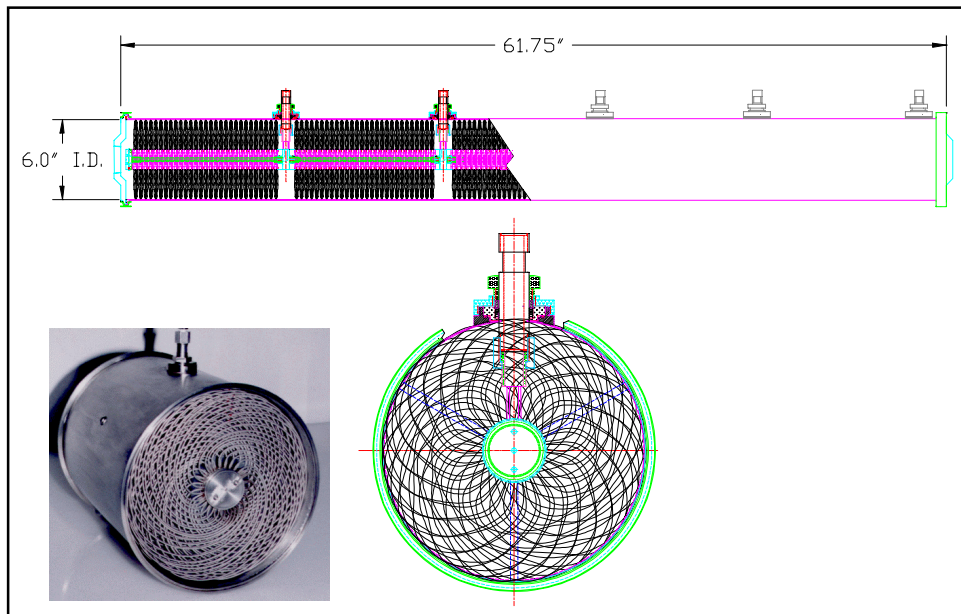
Two miniature heat exchanger configurations have been developed. The first resembles a conventional shell and tube heat exchanger with hydrogen and hydride alloy contained within stainless steel tubes and a water-ethylene glycol mix on the shell side (Figure 3). The shell is constructed of 2-inch diameter copper tubing with an expander at one end that mates with a 3-inch diameter stainless tube sheet. The heat exchanger contains approximately one hundred (100) 0.125-inch diameter, Type 304L stainless steel tubes. The hydrogen process boundary is

of all-welded construction. This configuration was selected for the initial thermal compressor design.



**Figure 3:** All-welded miniature hydride heat exchanger reduces compressor size and cost.

The second heat exchanger configuration employs Ergenics' ring manifold design, which permits a higher density tube arrangement for reduced size and weight (Figure 4). The tubes are joined to the central manifold via brazing. The ring manifold heat exchanger is the key to smaller and more cost effective compressors when production volumes increase.



**Figure 4:** Compact ring manifold hydride bed showing five stages in a single shell will further reduce size and cost. Inset shows a typical ring manifold heat exchanger.

## Operation to 5,000 psig

In a privately-funded project, Erganics built a single-stage, electrically-heated compressor with the following performance characteristics:

Inlet P - 300 psig  
Outlet P - 5,000 psig  
Inlet Flow - 5.5 std. l/m continuous  
Outlet Flow- 5.5 std. l/m average

The compressor employs a miniature hydride heat exchanger measuring 4 inches in diameter by 10 inches long depicted in Figure 5. Hydride alloy is contained within 0.125-inch diameter Inconel tubes. The heat exchanger is placed within an electrically heated furnace, which is cooled with ambient temperature air from a fan during absorption and periodically heated to 400°C to compress and release hydrogen. The hydride alloy was extensively tested after “soaking” at high pressure and temperature, with no disproportionation detected. (Disproportionation occurs when the elemental constituents of an alloy diffuse together and form stable, non-reversible hydrides.) Cycle time for absorption and desorption is relatively long at 16 minutes, because of heat transfer inefficiencies associated with air heating and cooling (rather than water).



**Figure 5:** Miniature Hydride Heat Exchanger for 5,000 psig Operation

A metal hydride inlet accumulator vessel accepts a continuous flow of inlet hydrogen at 300 psig. Periodically, hydrogen flows from the accumulator to the hydride heat exchanger during the absorption cycle.

Figure 6 plots furnace temperature, hydrogen pressure and outlet flow rate vs time for four thermal cycles. Outlet pressure was regulated by a valve. After each heating cycle, pressure was manually vented to 300 psig, accounting for the flow rate spikes at 1200, 2100, 3000 and 4000 seconds. During one test, pressure was increased to 6,000 psig. Testing of the electrically heated thermal compressor proved that hydrogen outlet pressures of over 5,000 psig are achievable with this technology. Achieving very high pressures in a multi-stage thermal compressor that uses only hot water as the energy source is a goal of our future work.



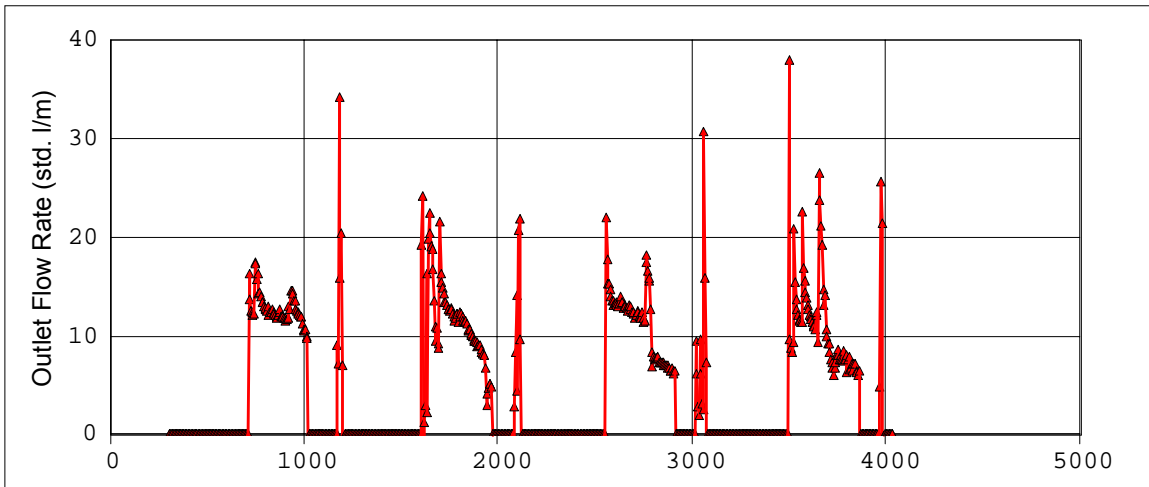
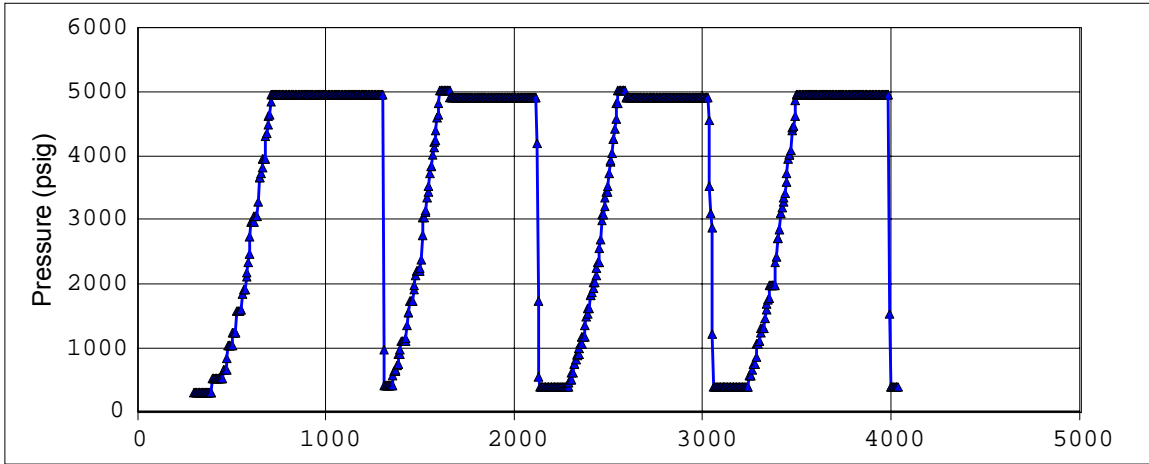
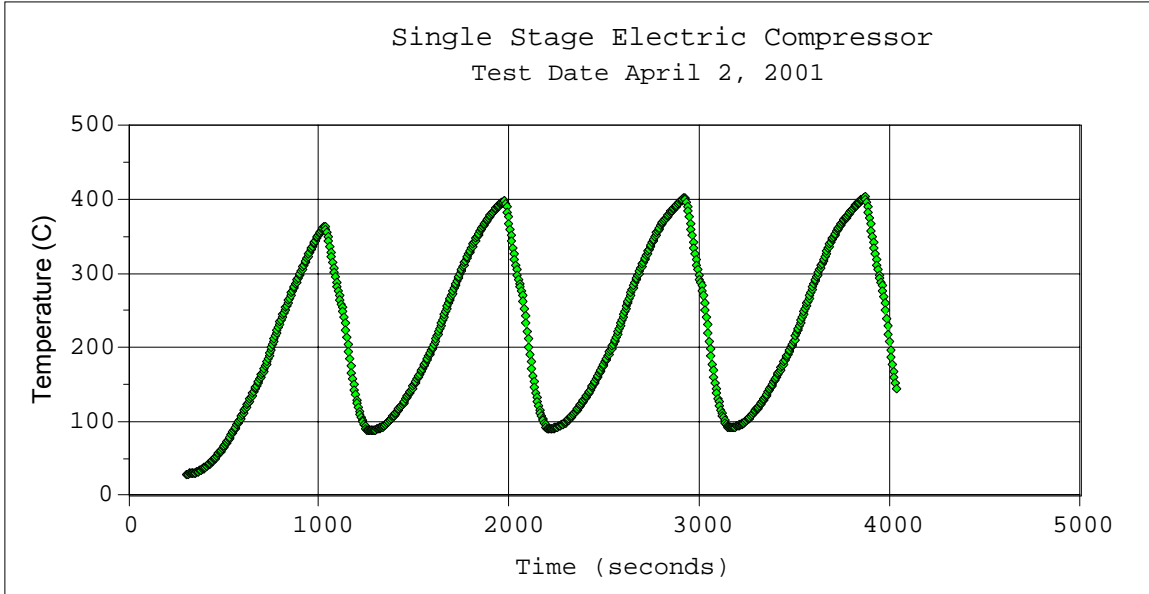


Figure 6: Thermal Compressor Operation at 5,000 psig

## **Future Work**

### **Removing or Tolerating Impure Gas Species**

In order to validate the conclusions reached to date, we plan to construct and demonstrate a single-stage thermal compressor that employs a miniature hydride heat exchanger and an associated test apparatus that will verify thermal compressor performance while processing hydrogen with impure gas species. The test apparatus will be flexible enough to vary inlet impurity levels to determine threshold contamination levels (levels at which compressor performance is affected). Three purification technologies will be demonstrated: passive purification for oxygen and water, inert gas purification, and elevated temperature desorption for CO and CO<sub>2</sub>.

### **Compression with Purification**

For impurities that can adversely affect fuel cell operation (e.g. nitrogen, CO), outlet hydrogen purity will be monitored to verify the degree to which a thermal compressor can perform the dual function of compressing and purifying hydrogen. This will allow the evaluation of trade-offs between hydrogen purity and compressor and fuel cell operating efficiencies necessary for the design and integration of full-scale systems.

### **Operation over 5,000 psig in a multi-stage, hot-water-powered compressor**

For high pressure operation over 5,000 psig, a suitable last-stage hydride alloy must be engineered and tested for long-term stability in the very high pressure environment. While anticipated operating temperatures of 90 to 110°C are modest for typical alloys, long term “soak” tests at pressures over 5,000 psig are warranted to assure alloy disproportionation is not encountered.

### **Process Validation**

The entire thermal compression process will be validated in a pilot-scale system that includes both the single stage (first stage) used for purification studies and subsequent stages needed to boost hydrogen pressure to over 5,000 psig. The flow rate capability of the pilot-scale system will be similar to that required for overnight refueling of a hydrogen fuel cell automobile.

## **Acknowledgement**

This material is based on work partially funded by the United States Department Of Energy’s Hydrogen Program under Cooperative Agreement No. DE-FC36-99GO10448.

## **References**

DaCosta, David H. 2000. “Advanced Thermal Hydrogen Compression.” In *Proceedings of the 2000 U.S. DOE Hydrogen Program Review*, 720-727. San Ramon, CA: NREL/CP-570-28890.

Eisenberg, F.G., Goodell, P.D. 1983. "Cyclic Response Of Reversible Hydriding Alloys In Hydrogen Containing Carbon Monoxide." *Journal of Less-Common Metals* 89: 55-62.

Golben, M., DaCosta, D.H. 1999. "Advanced Thermal Hydrogen Compression." In *Proceedings of the 34<sup>th</sup> Intersociety Energy Conversion Engineering Conference*. Warrendale, PA: SAE International.

Sandrock, G.D. 1997. "State of the Art Review of Hydrogen Storage in Reversible Metal Hydrides for Military Fuel Cell Applications," Office of Naval Research. Ringwood NJ: SunaTech, Inc.

Sandrock, G.D.; Goodell, P.D. 1984. "Cyclic Life of Metal Hydrides with Impure Hydrogen: Overview and Engineering Considerations." *Journal of Less-Common Metals* 104, 159-173.