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TWO-DIMENSIONAL DYNAMIC SIMULATION OF  
HYDROGEN STORAGE IN METAL HYDRIDE TANKS

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ABSTRACT

As proton exchange membrane fuel cell technology advances, the need for hydrogen storage intensifies. Metal hydride alloys offer one potential solution. However, for metal hydride tanks to become a viable hydrogen storage option, the dynamic performance of different tank geometries and configurations must be evaluated.

In an effort to relate tank performance to geometry and operating conditions, a dynamic, two-dimensional, multi-nodal metal hydride tank model has been created in Matlab-Simulink®. Following the original work of Mayer, Groll, and Supper<sup>1</sup> and the more recent paper from Aldas, Mat, and Kaplan<sup>2</sup>, this model employs first principle heat transfer and fluid flow mechanisms together with empirically derived reaction kinetics. Energy and mass balances are solved in cylindrical polar coordinates for a cylindrically shaped tank. The model tank temperature, heat release, and storage volume have been correlated to an actual metal hydride tank for static and transient adsorption and desorption processes.

The dynamic model is found to accurately predict observed hardware performance characteristics portending a capability to well simulate the dynamic performance of more complex tank geometries and configurations. As an example, a cylindrical tank filled via an internal concentric axial tube is considered.

MOTIVATION

There is a significant need for advanced hydrogen storage technologies to enable consideration of a hydrogen economy and enable the use of proton exchange membrane fuel cells in many applications. One such application considers the use of a fuel cell and hydrogen storage technology as an energy storage device in the place of batteries.

With the emergence of high power density and high performing fuel cells and electrolyzers, one can consider using fuel cells, electrolyzers and hydrogen storage in the place of rechargeable battery technology. This type of system may have unique advantages in comparison to current rechargeable batteries.

Unitized regenerative fuel cells (RFC) use a single anode/cathode electrode pair that is bi-functional, allowing

RFC operation in both electrolysis and fuel cell modes. This configuration is analogous to a rechargeable battery in that a single energy conversion unit can operate under both charging and discharging conditions. In electrolysis mode the RFC takes in electricity and water to produce hydrogen and oxygen. In fuel cell mode the RFC takes in hydrogen and oxygen (or air) to produce electricity and water. Regenerative fuel cells have a wide range of potential applications including energy storage devices coupled to renewable energy sources, power plants for automobiles and propulsion systems for satellites.<sup>3</sup> They are also being considered for use in NASA missions.<sup>4</sup>

The majority of large-scale practical applications that could benefit from RFC's currently utilize lead acid batteries. The main advantage of using lead acid batteries is that they are widely used and are therefore highly available, relatively well

understood, inexpensive and accepted by the public. Batteries are also efficient devices, achieving approximately 70-90% round trip efficiency. The main drawbacks of lead acid battery storage technology are (1) energy storage capacity that is proportional to battery size, (2) battery recharging duration, (3) short battery life as applied to residential duty cycles, and (4) hazardous waste handling during battery disposal.

The RFC or fuel cell electrolyzer system is unique when compared to traditional chemical batteries because the power capability, energy storage capacity, and recharge rate are all determined independently. With the exception of shared controls and plumbing, the hydrogen tank capacity solely determines the energy storage of the system, the fuel cell power output governs the power output of the system, and the electrolyzer power determines the "recharge" rate of the system. These properties lead to system advantages in specialized applications, particularly for those applications that require low to moderate power, and long duration performance. The fuel cell and electrolyzer can be sized as needed for the power requirement, while the hydrogen storage tank can simply be sized up or down, independently, to meet the energy storage requirement. A traditional chemical battery would require increases in all parameters in order to meet the demands of just one of these design criteria. Consequently, a fuel cell/electrolyzer system can theoretically achieve a better energy storage-to-volume ratio than even state-of-the-art chemical batteries<sup>5</sup>.

One particular application where the advantages of a fuel cell electrolyzer energy storage system are significant is the "silent watch" application required by the U.S. Army. The current research is being conducted to advance silent watch capability in a collaboration between the National Fuel Cell Research Center of U.C. Irvine, the U.S. Army Engineer Research and Development Center, and the Tank and Automotive Research and Development Center. The project is entitled Multi-Service Regenerative Electrolyzer Fuel Cell (MREF). The overall project includes the development and testing of a fuel cell, electrolyzer, and hydrogen storage system with Hydrogenics Corporation and the development of a dynamic model for understanding of such systems and development of controls for systems that incorporate fuel cells, electrolyzers and hydrogen storage. The goal is to eventually prove the performance of an MREF prototype sufficient to allow integration of such into a U.S. Army "Stryker" vehicle as manufactured in London, Ontario by General Dynamics Land Systems.

The current prototype system design is "charged" by supplying electrical power to an electrolyzer from the Stryker vehicle alternator during mobile operation. The electrolyzer breaks down water into hydrogen and oxygen. The oxygen is vented to the atmosphere and the hydrogen is stored. When power is needed from the system, the hydrogen is fed to the fuel cell where it is combined with air to produce electricity, heat and water exhaust.

Regenerative fuel cells are particularly well-suited to military applications because of the desire to use common fuels. Jet Propulsion 8, or JP-8, is a kerosene-based fuel which is the single battlefield fuel for Department of Defense applications including electric power generators, wheeled vehicles, aircraft, stoves, and heaters. The Navy uses JP-5 which is similar to JP-8. An immense logistical effort is needed to move the enormous quantities of JP-8 fuel required for military operations into a forward deployed overseas location. Delivered costs of JP-8 to Army combat platforms

have been estimated to be at least \$30-\$40/gallon for overland transport, and up to more than \$400/gallon for air delivery<sup>6</sup>.

Because of the "single battlefield fuel" mandate, fuel cell generators or other clean and efficient hydrogen consuming devices cannot be utilized on the battlefield unless the hydrogen is obtained from reformation of JP-8 or by other means with existing battlefield resources. Research and development has been performed with regards to JP-8 reforming, but a compact, reliable, sulfur tolerant JP-8 reformer has yet to be developed<sup>7,8</sup>. Electrolysis of water, on the other hand, could theoretically be utilized to obtain a source of hydrogen in forward deployed locations. Renewable sources of electricity such as wind and photovoltaics could be employed as the input source for the electrolyzer. Since most JP-8 electrical generators have excess capacity compared to the loads in the field they are serving, excess power from the generators could be utilized to electrolyze water to produce hydrogen. This scenario could have many benefits including reduced maintenance requirements and increased fuel efficiencies from the generators by operating them closer to their optimum setpoints.

If a practical and economical method for generating hydrogen in the field were available, a safe and efficient method of storing the hydrogen would also be required. Compressed hydrogen faces challenges with safety and volumetric storage efficiency. Cryogenic methods of storing hydrogen would be too energy intensive for a warfighter application. Metal hydrides could be a suitable method of hydrogen storage for applications where weight is not necessarily an issue (at forward base camps, for example.)

Disadvantages of any RFC or fuel cell electrolyzer system include: (1) low commercial availability, (2) complex systems that are currently not well understood, (3) the challenging hydrogen storage requirement, (4) limited hydrogen storage capacity of current technologies, (5) system safety and reliability, and (6) lower round-trip efficiencies.

Metal hydride storage tanks can potentially minimize some of these disadvantages. Metal hydride hydrogen storage is well-suited to the current application due to high volumetric storage density, which is required on-board the Stryker vehicle. A significant challenge for dynamic simulation of the system is the lack of a sufficiently resolved metal hydride dynamic model. In order to evaluate the performance of a fuel cell rechargeable energy system, to garner insight into the dynamic response characteristics of the system and individual components, and to design superior systems in the future, a dynamic model of metal hydride tank was developed. The dynamic model described in this paper is based on a bulk and geometrically resolved, first principles approach that solves the dynamic conservation of mass and conservation of energy equations together with appropriate calculations for heat transfer, and chemical and electrochemical reactions. The research includes evaluation of the dynamic model against measured metal hydride tank performance and extension of the model to investigate the potential performance of alternative metal hydride tank designs.

## EXPERIMENTAL DESCRIPTION

The test apparatus used in the experimental portion of this research consisted primarily of a small (approximately 1kg) Ergenics, Inc. aluminum tank containing Hydralloy C5 metal

hydride. To support the testing, an analog pressure gauge, two small manually operated needle valves, a digital temperature indicator with thermocouple, several feet of nylon tubing, a supply of research grade hydrogen gas regulated to 13.6 atm (200 psi), and a water bath were used. This equipment was configured as pictured in Figure 1.



Figure 1 Experimental test apparatus

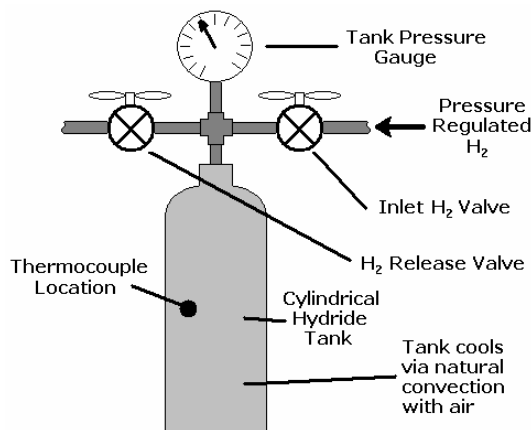


Figure 2 Configuration of naturally convected hydride tank testing

Figure 2 shows a schematic drawing of the experiment. All of the testing was conducted on a seasoned, previously used hydride tank. This ensured that minimal variation would be observed between tests. Testing was conducted by first measuring the initial mass of the tank to determine the starting quantity of hydrogen stored using a precision balance. With the hydrogen release valve closed, the inlet valve was then opened to allow hydrogen from a large gas cylinder to enter the tank at 13.6 atm. External tank temperature and internal tank pressure were recorded for the duration of the test. The mass of the tank was again measured at the end of the test to determine the total mass of hydrogen stored. The tank was emptied by closing the inlet valve and opening the hydrogen release valve after each test.

Tests were also conducted with the tank cooled by a circulating water bath, pictured in Figure 1 and shown schematically in Figure 3. The procedure was identical to the air-cooled test, with the exception that the tank was submerged in a continuously circulating water bath.

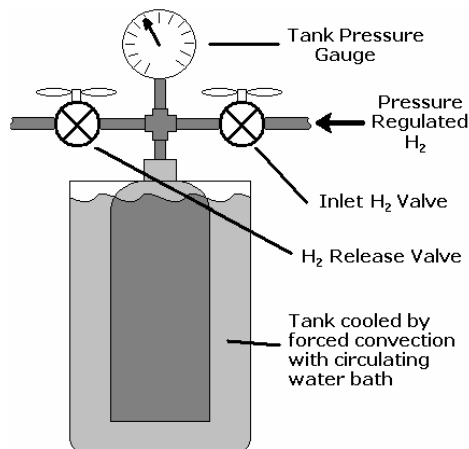


Figure 3 Diagram showing water cooled test apparatus

### MODEL DESCRIPTION

Closely following the work of Aldas, Mat, and Kaplan<sup>2</sup>, the hydride tank model employed in this work determines the tank temperature, the quantity of energy released, and the mass of hydrogen absorbed within each node of a discretized model when given local operating conditions such as temperature, heat transfer rates, and hydrogen inlet pressure. This is accomplished by simultaneously solving the conservation of mass and conservation of energy equations for the gaseous hydrogen and the solid metal alloy in each of the discrete nodes of the model. The baseline model is discretized into 10 cylindrical nodes as shown in Figure 4. Hydrogen can only enter or exit the tank through the upper surface of the tank in a manner that physically represents the inlet of the experimental hydride tank.

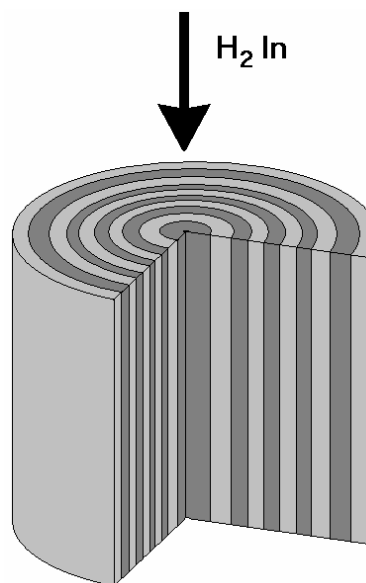


Figure 4 Cross sectional schematic view of model nodal discretization

## Hydrogen Conservation of Mass

The volume of hydrogen gas in each node is equal to the porous space within the node,

$$V_g = \varepsilon V_{node} \quad (1)$$

where  $\varepsilon$  is the porosity of the metal alloy. The mass of hydrogen within a node can change due to advection, or via the sorption reaction with the metal alloy. The mass conservation equation can therefore be written as,

$$\frac{\partial m_g}{\partial t} = \dot{m}_{in} - \dot{m}_{out} - \dot{m}_{reaction} \quad (2)$$

The mass flow rates in or out,  $\dot{m}_{in}$  and  $\dot{m}_{out}$ , respectively, are found by first using Darcy's Law<sup>9</sup> to determine the gas velocity,  $V_g$  :

$$V_g = -\frac{k}{\mu} \frac{\partial P}{\partial x} \quad (3)$$

and then using the gas velocity to determine flow rate by multiplying by adjacent nodal surface area and gas density,

$$\dot{m}_{in} = V_g \rho_g A \quad (4)$$

The rate of hydrogen sorption reaction,  $\dot{m}_{reaction}$ , can be found empirically as described later. Having determined the rates of gases entering, exiting, and reacting within a node, equation (2) can be numerically integrated to find the instantaneous mass of gaseous hydrogen in the control volume.

## Solid Alloy Conservation of Mass

The volume of solid hydride alloy within a node is equal to the non-porous volume of the node:

$$V_s = (1 - \varepsilon) V_{node} \quad (5)$$

The mass of the solid can only change by absorbing or desorbing hydrogen. The conservation equation is consequently written as:

$$\frac{\partial m_s}{\partial t} = \dot{m}_{reaction} \quad (6)$$

## Hydrogen Conservation of Energy

The gaseous energy of each node can change by four processes:

1. Conduction with gas in surrounding nodes
2. Convection between gas and the solid alloy
3. Change in mass due to the sorption process
4. Advection (gas transport) with surrounding nodes

These four transfer methods are accounted for in the following gaseous energy conservation equations:

$$\frac{\partial E_g}{\partial t} = -k \frac{\partial T_g}{\partial x} + hA(T_s - T_g) + \dot{m}_{in} h_{in} - \dot{m}_{out} h_{out} \quad (7)$$

Where the change in energy can be written as:

$$\frac{\partial E_g}{\partial t} = \frac{\partial(\rho_g V_g C_p T_g)}{\partial t} \quad (8)$$

The nodal hydrogen temperature can be determined by combining equations (7) and (8) and numerically integrating over time.

## Solid Alloy Conservation of Energy

The change in energy of the solid alloy in each node is due to four processes:

1. Conduction with solid in surrounding nodes
2. Convection with hydrogen gas within node
3. Heat release or supply during the sorption reaction
4. Mass change via hydrogen sorption

The energy conservation equation for the solid within each node is therefore:

$$\frac{\partial E_s}{\partial t} = -k \frac{\partial T}{\partial x} + hA(T_s - T_g) + \dot{m}_{reaction} \Delta H \quad (9)$$

where, as before, the rate of change of solid energy can be written as:

$$\frac{\partial E_s}{\partial t} = \frac{\partial(\rho_s V_s C T_s)}{\partial t} \quad (10)$$

The nodal solid temperature can be found by combining (9) and (10) and numerically integrating.

## Rate of Hydrogen Reacting

The rate at which hydrogen gas is absorbed or desorbed can be modeled by the following empirical equation<sup>1</sup>:

$$\dot{m}_{reaction} = -C_a e^{\left(\frac{-E_a}{RT}\right)} \ln\left(\frac{P_g}{P_{vH}}\right) (\rho_{full} - \rho_{node}) V_s \quad (11)$$

Where  $C_a$  is the reaction rate constant,  $E_a$  is the activation energy,  $R$  is the ideal gas constant, and  $\rho_{full}$  and  $\rho_{node}$  are the saturated and nodal densities of the solid alloy, respectively.  $P_g$  is the hydrogen pressure within the node and  $P_{vH}$  is the pressure predicted by the van't Hoff equation<sup>10</sup>,

$$\ln(P_{vH}) = \frac{\Delta H}{RT_g} - \frac{\Delta S}{R} \quad (12)$$

The values of enthalpy of reaction,  $\Delta H$ , and the change in entropy for the reaction,  $\Delta S$ , are experimentally determined for the given hydride alloy being used.

## MODEL EVALUATION BY DATA COMPARISON

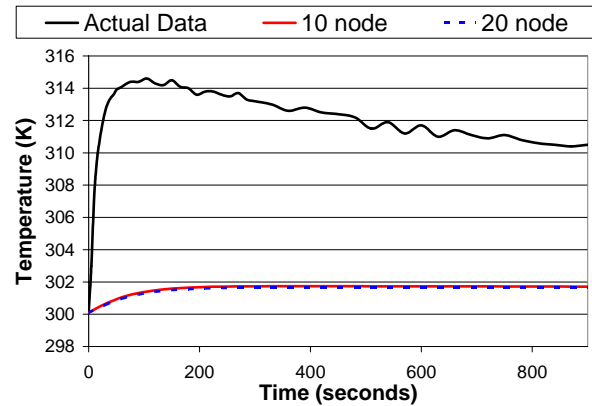
Hydride tank model simulations were performed with material properties and physical values matching the actual experiment as closely as possible. The model parameter values, as shown in Table 1, were garnered from material property databases, manufacturer specifications, and published work. Manufacturer and online data presented are for the actual alloy used in testing, Hydralloy C5. Published data is for a similar  $AB_2$  alloy,  $TiMn_{1.5}$ .

**Table 1. Model parameter values and sources**

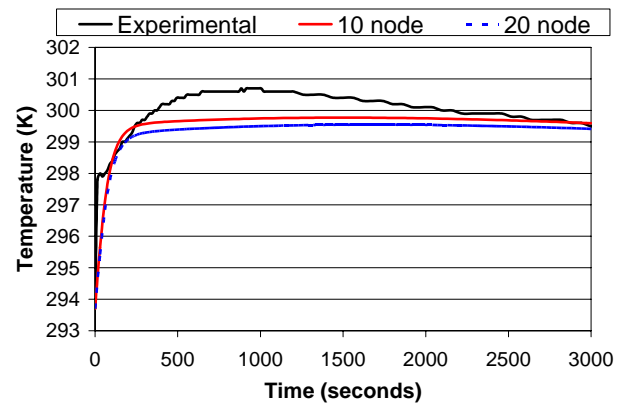
Property	Value	Source
$\Delta H$	$-27.4 \text{ kJ/mol}$	Online data base <sup>11</sup>
$\Delta S$	$-0.112 \text{ kJ/molK}$	Online data base <sup>11</sup>
$C_a$	$833 \text{ s}^{-1}$	Published paper <sup>12</sup>
$E_a$	$29651 \text{ J/mol}$	Published paper <sup>12</sup>
$C$	$418.7 \text{ J/kgK}$	Manufacturer specifications <sup>13</sup>
$k$	$1.0 \text{ W/mK}$	Published paper <sup>14</sup>

The first simulation mimicked the first physical test in which the tank was filled with pure hydrogen at 13.6 atm while the tank was cooled only by natural convection with the surrounding air. As shown in Figure 5, the model utilizing reference  $\Delta H$  and  $\Delta S$  values under predicts tank temperature for both 10 and 20 node models. In the experiment, the actual tank absorbed 1.31 grams of hydrogen, while the 10 node model predicted absorption of just 0.21 grams and the 20 node model predicted 0.20 grams. These are clearly poor results. However, since some of the model parameters were estimated from literature sources that are not directly applicable to the current metal hydride, this disagreement is not unexpected.

Figure 6 shows results for filling the tank while it is cooled by a water bath. Again, the same reference values are used resulting in a poor outcome. For this case, the actual



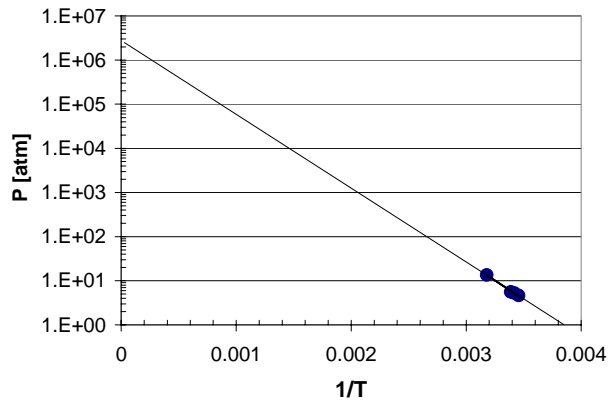
**Figure 5. Comparison between experimental and model temperature results for air cooled tank using reference values for enthalpy and entropy of reaction**



**Figure 6 Comparison between experimental and model temperature results for water-cooled tank using reference values for enthalpy and entropy of reaction**

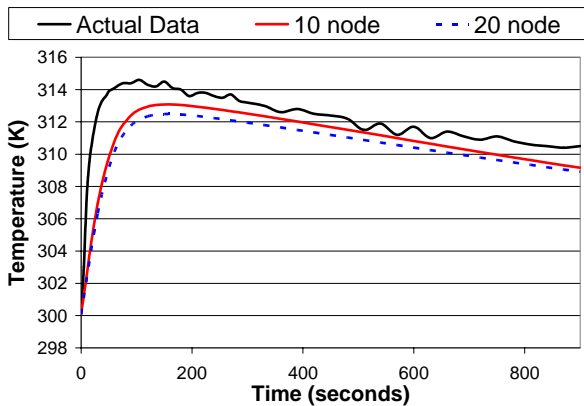
tank absorbed 3.1grams of hydrogen while both models predicted 1.4 grams.

As a result of findings presented in Figure 5 and Figure 6 it was decided that use of the current literature model parameters was not justified. Instead of using the reference values of Table 1 for the enthalpy and entropy of reaction, these values can be calculated experimentally using the van't Hoff equation (12) for a specific single set of experimental conditions. On a plot of  $\ln(P)$  versus  $1/T$ ,  $\Delta H$  can be calculated from the slope of the line, and  $\Delta S$  is found from the y-intercept. Data collected for the tank used in this testing is presented in Figure 7 in this manner.



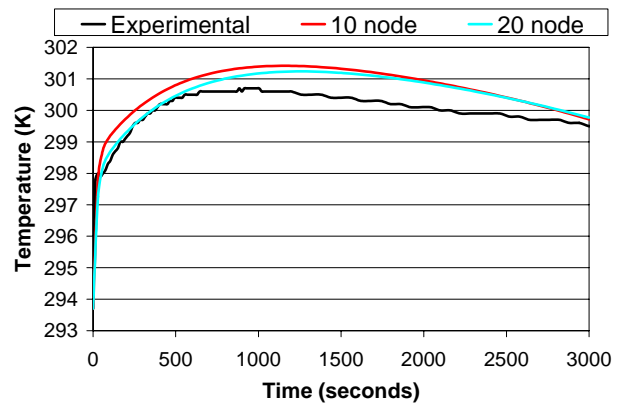
**Figure 7** Plot showing extrapolation of experimental data used to determine enthalpy and entropy change for the current hydride reaction

Experimentally determined entropy and enthalpy values are calculated as 28800 J/mol and 112.2 J/molK, respectively. Using these values, the model more accurately reproduces experimental results. The 10 node model fills with 1.4 grams of hydrogen and the 20 node model absorbs 1.3 grams. The temperature versus time plots for both models are shown in Figure 8. Note that these dynamic model predictions much better approximate the experimental observations.



**Figure 8.** Comparison between experimental and model temperature results for air cooled tank using experimental values for enthalpy and entropy of reaction

Model results for the water cooled tank scenario also show improvement when using the experimentally determined values for enthalpy and entropy of reaction over those from published databases. The 10 and 20 node models both predicted 3.1 grams of hydrogen absorption and the dynamics of the tank temperature response are well predicted by the model, especially using the 20-node model, as shown in Figure 9.

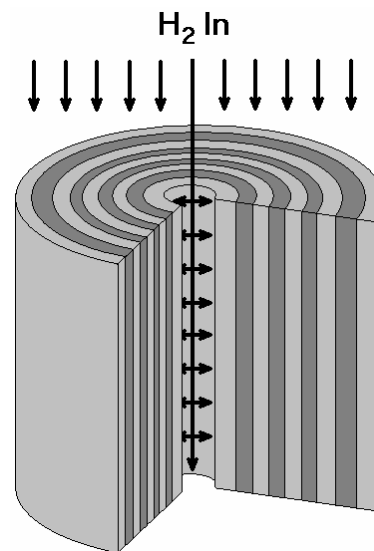


**Figure 9.** Comparison between experimental and model temperature results for water-cooled tank using experimental values for enthalpy and entropy of reaction

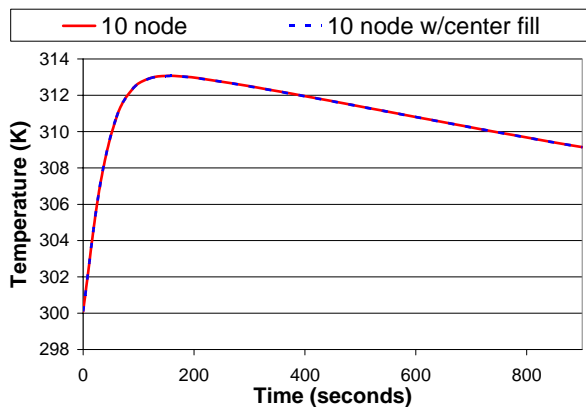
## ALTERNATIVE TANK CONFIGURATION

### Tank Filled Via Internal Axial Tube

An interesting and fairly simple modification can be made to the original hydride tank model to provide for faster hydrogen sorption by increasing the surface area available for filling. Instead of allowing hydrogen to enter the tank only through the upper surface of each node, an internal axial tube can be used in the center of the tank, as shown in Figure 10. The model results of this tank scenario, for an open air fill, are shown in Figure 11 compared with those of the standard tank. Though the graphs of temperature versus time for both tanks are very similar, the tank containing the center axial tube actually absorbed 1.6 grams of hydrogen compared to the 1.4 grams of the standard tank, resulting in a 14% improvement.

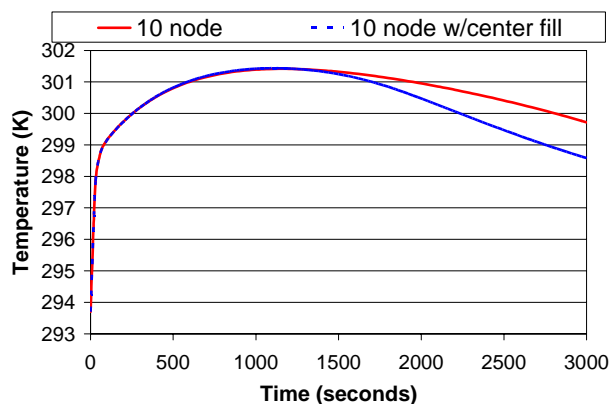


**Figure 10** Diagram of modified, axially filled hydride tank



**Figure 11 Comparison between standard and modified tank models for air cooled scenario**

The filling results also change for a tank with an axial center tube when cooled by water. Instead of absorbing more hydrogen as in the air cooled case, the modified water cooled tank still absorbed 3.1 grams during the 3000 second test. However, the tank absorbed the hydrogen more quickly. The modified tank, with center fill tube, was completely filled (3.1 grams) in just 2100 seconds, whereas the normal tank required a full 3000 seconds to reach the maximum capacity. This difference resulted in the more rapid post-fill cooling observed in Figure 12. This is a 30% reduction in fill time.



**Figure 12 Comparison between standard and modified tank models for water cooled scenario**

## CONCLUSIONS

A dynamic nodal model of a metal hydride hydrogen storage tank has been developed and evaluated against measured performance of a cylindrical storage tank. Comparison to data shows that the model and approach well approximate observations. As such, this proven dynamic model is shown to be useful for evaluating metal hydride tank design and performance. One simple change in tank design was investigated leading to 14% more hydrogen stored in the air-cooled case, or a 30% faster fill in the water-cooled case. The current dynamic model can assist in tank design for a particular application leading to improvements in performance. The current approach is simple enough that

dynamic hydride tank modeling can be further applied to integrated regenerative fuel cell systems.

<sup>1</sup> U. Mayer, M. Groll, W. Supper, Heat and Mass Transfer in Metal Hydride Reaction Beds: Experimental and Theoretical Results, *Journal of the Less-Common Metals*, 1987; 131; 235-244.

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<sup>9</sup> A. Jemni, S. Ben Nasrallah, Study of Two-Dimensional Heat and Mass Transfer During Absorption in a Metal-Hydrogen Reactor, *International Journal of Hydrogen Energy*, 1995; 20; 43-52.

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<sup>12</sup> S. Suda, N. Kobayashi, Reaction Kinetics of Metal Hydrides and Their Mixtures, *Journal of Less-Common Metals*, 1980;73;119-126.

<sup>13</sup> Ergenics, Inc. (manufacturer).

<sup>14</sup> S. Suda, N. Kobayashi, Thermal Conductivity in Metal Hydride Beds, *International Journal of Hydrogen Energy*, 1981; Vol. 6, No. 5; 521-528.