

### VI.F.3 System-Level Analysis of Hydrogen Storage Options

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#### **Objectives**

- Model various developmental hydrogen storage systems.
- Analyze hybrid systems that combine features of more than one concept.
- Develop models to “reverse-engineer” particular approaches.
- Identify interface issues, opportunities and data needs for technology development.

#### **Technical Barriers**

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Weight and Volume
- C. Efficiency
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- Q. Thermal Management
- R. Regeneration Processes
- T. Heat Removal

#### **Approach**

- Develop thermodynamic and kinetic models of processes in complex metal hydride, carbon, and chemical hydrogen storage systems.
- Assess improvements needed in material properties and system configurations to achieve hydrogen storage targets.

#### **Accomplishments**

- Developed a model that considers thermodynamics, sorption kinetics and energetics of hydrogen storage in sodium alanates.
- Validated the sodium alanate model against the available experimental data.
- Used the validated model to conduct a critical evaluation of the alanate system with regards to meeting DOE targets for recoverable hydrogen, discharge rate, refueling rate and H<sub>2</sub> delivery pressure.
- Developed a model for hydrogen storage in activated carbons at low temperatures and medium pressures.

- Used the model to determine conditions and technology improvements needed for the activated carbon system to satisfy the early DOE targets for hydrogen storage.

### Future Directions

- Verify hydrogen storage capacity in activated carbon.
- Verify sorption kinetics for sodium alanates.
- Conduct sensitivity analysis and include coupled parameters.
- Develop a modeling tool that material developers can use to determine properties needed to meet storage targets.
- Analyze life-cycle efficiency of chemical hydrogen storage systems.

### Introduction

Several different approaches are being pursued to develop on-board and off-board hydrogen storage materials, processes, and technologies. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces between the storage system and the fuel supply system on the one hand and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on these approaches and to evaluate their potential in meeting the DOE targets for on-board applications.

### Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the hydrogen storage systems being developed under DOE sponsorship, and use them to identify significant component and performance issues and assist DOE and its contractors in evaluating alternative system configurations and design operating parameters. We will establish performance criteria that may be used, for example, in developing storage system cost models. The models will be refined and validated as data become available from the various developers. We have formed a Storage Analysis Working Group to coordinate our research activities with other analysis projects (such as those being conducted by TIAX, Gas Technology Institute, and the Centers of Excellence) to assure consistency and avoid

duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and hydrogen user (fuel cell or internal combustion engine hydrogen vehicles for on-board systems, on-board hydrogen storage subsystems associated with off-board storage systems).

### Results

We formulated a model for hydrogen storage in sodium alanates by considering the thermodynamics of the  $\text{NaAlH}_4\text{-Na}_3\text{AlH}_6\text{-NaH}$  system [1]. We derived a first-order kinetics model for absorption and desorption reactions by analyzing the data measured by Sandrock, Gross and Thomas [2]. We developed a transient thermal model to calculate the temperatures of the various components of the storage system, hydrogen pressure, and hydrogen flow rate into and out of the system.

The model was used to analyze a metal hydride (MH) media (see Figure 1) in the form of a powder packed inside nominally 4-wt%, 40-PPI (pores per inch) Al 2024 alloy foam to compensate for the poor

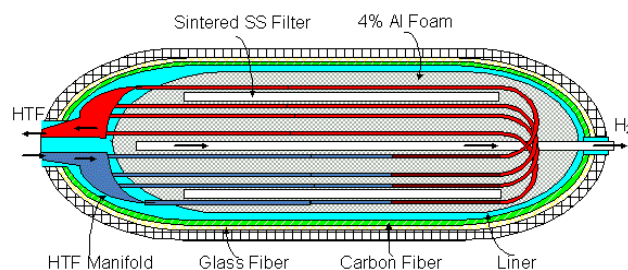


Figure 1. Metal Hydride Tank, Adapted From Lasher [3]

thermal conductivity of the MH powder (0.25-0.5 W/m.K). The tube-sheet plenums (304 SS, 0.9 mm sheet thickness) for distributing and collecting the heat transfer fluid (HTF) are inside the head space of the tank, joined by U-tubes embedded in the foam. The composite tank consists of 2.4-mm T700S carbon fiber, wound on a 2-mm thick stainless steel (304 SS) metal liner, encased in 2.5-mm Eglass glass fiber [3].

We considered that hydrogen is desorbed using the sensible heat in the ethylene-glycol fuel cell stack coolant at 115°C. Because the minimum tank pressure is 3-8 bar, whereas the plateau pressure for  $\text{Na}_3\text{AlH}_6$  dissociation is 1.7 bar at 115°C, only the first dehydrogenation step can be carried out. Thus, the  $\text{H}_2$  storage capacity of the MH media is theoretically limited to 3.7 wt%. Under transient conditions, the tank pressure can reach 24.4 bar – the plateau pressure for  $\text{NaAlH}_4$  dissociation at 115°C.

We considered that the MH is charged with  $\text{H}_2$  at 100 bar. During charging, the MH medium can reach a peak temperature of 169.4°C, which is the temperature corresponding to 100-bar plateau pressure for hydrogenation of  $\text{Na}_3\text{AlH}_6$  to form  $\text{NaAlH}_4$ . For reasonable refueling times, we strive to limit the peak MH temperature to 165°C since the absorption rate decreases with temperature above 165°C and approaches zero at 169.4°C.

A multi-dimensional non-linear equation solver based on steepest descent/quasi-Newton update technique was used in conjunction with the MH model to simultaneously satisfy the system requirements. The tank volume was calculated so that there is sufficient MH for storing 5.6 kg of recoverable  $\text{H}_2$  – the amount needed in a family-sedan fuel cell vehicle for 360-mile driving range [4]. The maximum allowable depth of discharge (DOD) of MH was determined such that the MH medium has the ability to supply 1.6 g/s of  $\text{H}_2$  (for the 80-kWe fuel cell system), on demand, even under least favorable conditions (MH at maximum DOD and cover gas at minimum delivery pressure). For first-order reaction kinetics, the charging rate decreases with the number of moles of  $\text{Na}_3\text{AlH}_6$  remaining. Thus, the maximum allowable state of charge (SOC) was determined so as to satisfy the minimum refueling rate criterion. The number of heat

exchange U tubes was calculated so as to limit the peak MH temperature during refueling to 165°C. The peak heat load condition is encountered during refueling of the MH medium that has been depleted to its maximum allowable DOD. The coolant flow rate during refueling was calculated so as to have a 5°C temperature rise across the inlet and outlet manifolds. The temperature of the coolant at inlet was assumed to be 100°C.

Our model indicates that a MH tank that satisfies the above requirements would weigh >800 kg and occupy >600 L. The maximum DOD has to be restricted to 59.6% in order to meet the criterion of minimum full-flow rate of  $\text{H}_2$ . Within this envelope of operating conditions, only 54.6% of  $\text{H}_2$  is recoverable, and the recoverable  $\text{H}_2$  fraction in the MH media is 1.4%. The usable specific energy is 0.23 kWh/kg (0.007 kg  $\text{H}_2$  /kg), and the usable energy density is 0.28 kWh/L (0.009 kg  $\text{H}_2$ /L). Both are well short of the DOE 2007 targets. We calculate that the peak heat load during refueling is 993 kW and that 258 U tubes are needed to limit the MH medium temperature to 165°C.

A parametric study was conducted to determine the enhancement in desorption kinetics needed to increase the recoverable  $\text{H}_2$  fraction to 90% of the theoretical capacity (3.6% under our operating conditions). The results, summarized in Table 1, indicate that the recoverable  $\text{H}_2$  fraction improves to 82.7% with a five-fold enhancement and to 88.4% with a ten-fold enhancement in desorption kinetics. The maximum DOD increases to 87.7% with a five-fold enhancement and to 93.6% with a ten-fold enhancement in desorption kinetics. The corresponding reduction in tank weight and volume are 28% and 34%, respectively.

Two of the many reasons for not realizing the full 3.6 wt% H capacity of the MH medium are production of NaCl during feed preparation and loss of capacity because of feed impurities, imperfect handling and non-uniform Ti distribution. Our calculations show that the MH medium weight can be reduced by 23% and the tank weight by about 14% if the inerts are removed from the system.

The importance of contact resistance between foam and heat transfer tubes was investigated by

**Table 1.** Effect of Desorption Kinetics on H<sub>2</sub> Recoverability

		Desorption Kinetics			DOE 2007 Target
		1X	5X	10X	
Recoverable H <sub>2</sub> in NaAlH <sub>4</sub>	%	54.6	28.7	88.4	90
SOC, Min/Max	%	40.4/95	12.3/95	6.6/95	
H <sub>2</sub> Refueling Rate	g/min	990	860	840	500
Weight of MH	kg	400	264	247	
Tank Weight	kg	813	613	588	125
Tank Volume	L	656	457	341	155
Recoverable H <sub>2</sub> in MH	kg H <sub>2</sub> /kg %	1.4	2.1	2.3	
Recoverable H <sub>2</sub> in Tank	kg H <sub>2</sub> /kg %	0.7	0.9	1.0	4.5
Specific Energy	kWh/kg	0.23	0.30	0.32	1.5
Energy Density	kWh/L	0.28	0.41	0.43	1.2

running a parametric calculation in which the contact resistance was arbitrarily reduced to one-tenth its value (equivalent to increasing the associated heat transfer coefficient  $h_c$  by a factor of ten). The results of this calculation, which also assumes a ten-fold enhancement in desorption kinetics and removal of inerts, are summarized in Table 2. These results show that a ten-fold decrease in contact resistance results in a 38% reduction in the required number of

heat transfer tubes and about a 17% reduction in the overall weight of the tank.

Another calculation was run in which the material of the liner, manifold and heat transfer tubes was changed to the lighter Al 2024 alloy. The substitution results in a 5% reduction in the required number of heat transfer tubes and a 22% reduction in tank weight. This system achieves a specific energy

**Table 2.** Effect of Heat Transfer on Specific Energy and Energy Density

10X Desorption Kinetics No Inerts		1X $h_c$ SS HX	10X $h_c$ SS HX	10X $h_c$ Al HX	DOE 2007 Target
Recoverable H <sub>2</sub> in NaAlH <sub>4</sub>	%	87.9	88.4	88.4	90
SOC, Min/Max	%	7.1/95	6.6/95	6.6/95	
H <sub>2</sub> Refueling Rate	g/min	840	840	840	500
Number of HX Tubes		280	175	166	
Weight of MH	kg	192	191	191	
Tank Weight	kg	506	421	328	125
Tank Volume	L	350	323	321	155
Recoverable H <sub>2</sub> in MH	kg H <sub>2</sub> /kg %	2.9	2.9	2.9	
Recoverable H <sub>2</sub> in Tank	kg H <sub>2</sub> /kg %	1.1	1.3	1.7	4.5
Specific Energy	kWh/kg	0.37	0.44	0.57	1.5
Energy Density	kWh/L	0.53	0.58	0.58	1.2

of  $<0.6$  kWh/kg, which is 63% lower than the 2007 target, and an energy density of 0.6 kWh/L, which is 50% of the 2007 target.

The effect of improved thermal conductivity of the heat transfer support was investigated by analyzing a system with 6-wt% Al foam. The results indicate an 18% reduction in the required number of heat transfer tubes with 6-wt% Al foam because of the improved heat transfer characteristics. The reduction in the weight of the heat transfer tubes is nullified, however, by the corresponding increase in the weight of the foam.

Anton et al. [5] have measured the packing density of the MH powder inside Al foam under different conditions. Their data indicate a packing density of  $580 \text{ kg/m}^3$  with tap consolidation,  $800 \text{ kg/m}^3$  with tamp consolidation, and  $970 \text{ kg/m}^3$  with compaction at a gas pressure of 100 bar. Our model indicates that increasing the packing density to  $800 \text{ kg/m}^3$  from  $580 \text{ kg/m}^3$  results in only an 8% decrease in tank weight but a 40% reduction in tank volume. Increasing MH packing density to  $970 \text{ kg/m}^3$  results in an additional decrease of 4% in tank weight and 10% in tank volume. With pressure compaction, the system achieves 40% of the 2007-target specific energy and 60% of the target energy density.

The minimum delivery pressure to meet the DOE targets decreases from 8 bar in 2007 to 4 bar in 2010 and to 3 bar in 2015. We used our model to ascertain the effect of the minimum delivery pressure on the tank weight and volume and found that it has only a small effect on the size of the hydrogen storage system.

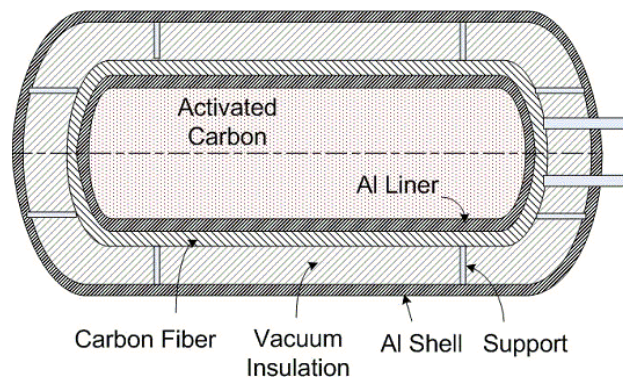
We also used our model to calculate the effect of  $\text{H}_2$  refueling rate on the performance of the storage system. The maximum SOC and the maximum DOD both decrease with increase in refueling rate. Thus, raising the  $\text{H}_2$  refueling rate from 0.5 to 1 kg/min reduces the recoverable hydrogen fraction from 92.4% to 85.6%. The recoverable hydrogen fraction further decreases to 76% if the refueling rate is increased to 1.5 kg/min.

In FY 2005, we also investigated hydrogen storage in activated carbon at low temperatures (77-150 K) and medium pressures ( $<100$  bar). We determined hydrogen uptake in activated carbon

(AC) from Ono-Kondo theory for adsorption isotherms and model parameters derived by Benard and Chahine [5], and hydrogen storage in the void space from the Lee-Kesler equation of state. We assumed that AC is contained within a thermally insulated, filament-wound carbon fiber pressure vessel with a 2-mm Al liner and 3-mm outer Al shell (see Figure 2). The thickness of the multi-layer vacuum superinsulation ( $10^{-5}$  torr pressure) vessel was determined to limit the heat transfer rate from the vessel to 1 W and of T700 carbon fiber to provide a 2.25 safety factor at 100 bar maximum pressure.

Figure 3 presents some preliminary results on the effects of storage pressure, minimum delivery pressure and temperature swing on the system storage density and weight. It shows that at 150 K, AC does not meet the 2007 targets of 4.5 wt% ( $1.5 \text{ kWh/kg}$ ) or  $36 \text{ kg/m}^3$  ( $1.2 \text{ kWh/L}$ )  $\text{H}_2$  storage density. With a 50-K temperature swing, it may be possible to meet the weight but not the volume target at  $>100$  bar storage pressure and  $<4$  bar minimum delivery pressure.

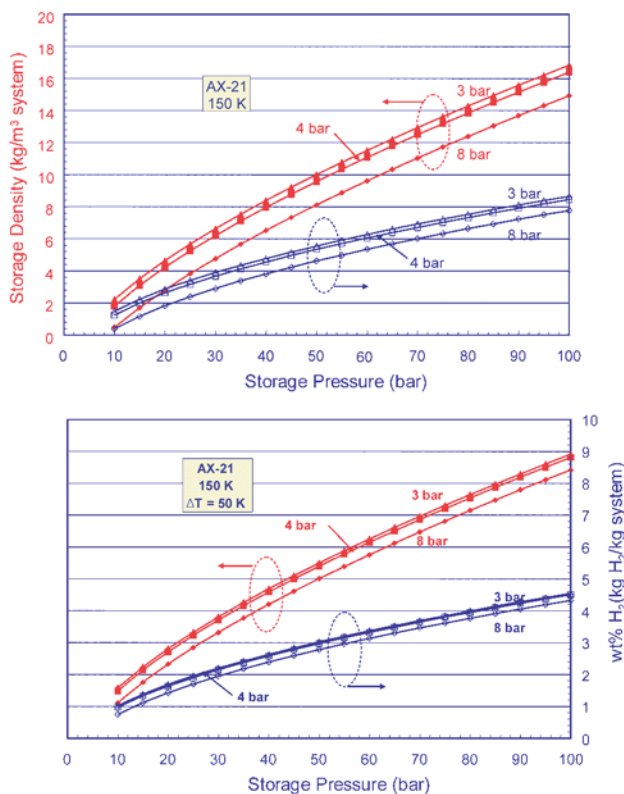
Table 3 summarizes the extent to which the DOE 2007 targets can be met with commercially available AX-21 ( $300 \text{ kg/m}^3$  bulk density). It indicates that at 77 K, it may be possible to meet the 4.5-wt% target with 50-K temperature swing at 50 bar or isothermally at 100 bar. At 150 K, the maximum  $\text{H}_2$  storage density is  $<30 \text{ kg/m}^3$ . Densifying AX-21 to  $700 \text{ kg/m}^3$  bulk density invariably results in loss of storage capacity. Table 3 also indicates the effort needed to develop engineered activated carbons that satisfy the 2007 targets at various operating



**Figure 2.** Activated Carbon Storage System

**Table 3.** Achievable Performance of Activated Carbons

T (K)	P (bar)	$\Delta T$ (K)	AX-21		Densified AX-21		EAC-07	
			wt% H <sub>2</sub>	kg/m <sup>3</sup>	wt% H <sub>2</sub>	kg/m <sup>3</sup>	wt% H <sub>2</sub>	kg/m <sup>3</sup>
77	50	0	3.2	11.6	1.6	10.6		
77	50	50	5.0	19.5	3.2	23.0	4.5 <sup>2</sup>	36
77	100	0	5.4	21.7	2.5	17.4		
77	100	50	7.1	29.6	4.1	29.9	4.5 <sup>1</sup>	36
150	50	0	2.3	8.1	1.4	9.4	4.5 <sup>6</sup>	36
150	50	50	2.8	10.0	1.8	12.4	4.5 <sup>5</sup>	36
150	100	0	3.9	14.9	2.2	15.8	4.5 <sup>4</sup>	36
150	100	50	4.3	16.8	2.6	18.8	4.5 <sup>3</sup>	36

**Figure 3.** Performance of Activated Carbon Storage System at 150 K

conditions. Here, the superscript 1 denotes the least and 6 the most development effort needed.

### Conclusions

- The usable H<sub>2</sub>-storage capacity of a metal hydride is determined not only by the stoichiometry and thermodynamics but also

sorption kinetics. Obtaining 90% H<sub>2</sub> recovery will require a ten-fold or greater improvement in the published desorption kinetics of NaAlH<sub>4</sub> catalyzed with 4% Ti. The kinetics can be enhanced by increasing the Ti content, but the theoretical H capacity suffers with addition of Ti.

- Even though the required H<sub>2</sub> absorption rate (8-25 g/s) is much higher than the minimum peak desorption rate (1.6 g/s for an 80-kW fuel cell system), the absorption kinetics are less of a challenge because hydrogen can be absorbed at higher temperatures. The allowable absorption temperature is limited either by the H<sub>2</sub> source pressure or by the melting point of NaAlH<sub>4</sub>. At 100-bar H<sub>2</sub> supply pressure, the allowable MH media temperature is 169.4°C.
- Cooling the MH during refueling is a difficult task but is not regarded as a show stopper. Depending on the refueling rate, the peak cooling rate can exceed 1 MW. Because the MH powder has poor thermal conductivity, a support, such as metal foam, is needed to aid in heat removal. The total cooling load is more than 100 MJ for a storage system with 5.6 kg of recoverable H<sub>2</sub>. An off-board coolant and a secondary heat dissipation system will likely be needed.
- It may be possible to meet the DOE 2007 target for specific energy (1.5 kWh/kg) with activated carbon at 77-150 K and pressure <100 bar with or without temperature swing. Additional material development is needed to achieve the energy density target of 1.2 kWh/L.

**FY 2005 Publications/Presentations**

1. R. K. Ahluwalia and R. Kumar, "Metal-Hydride Hydrogen Storage for Automotive Fuel Cell Systems," *Hydrogen Storage Systems Analysis Meeting*, Washington, DC, March 29, 2005.
2. R. K. Ahluwalia and J-C Peng, "High-Pressure, Low-Temperature Storage of Hydrogen on Activated Carbon," *Hydrogen Storage Systems Analysis Meeting*, Washington, DC, March 29, 2005.
3. R. K. Ahluwalia and R. Kumar, "Metal Hydride Hydrogen Storage System for Automotive Fuel Cell Systems," *NHA Annual Hydrogen Conference 2005*, Washington, DC, March 29 – April 1, 2005.
4. R. K. Ahluwalia, J-C Peng, and R. Kumar, "System Level Analysis of Hydrogen Storage Options," *Hydrogen Storage Tech Team Meeting*, Southfield, MI, April 21, 2005.
5. R. K. Ahluwalia, "Hydrogen Storage System Analysis Tool," *Workshop on Hydrogen Storage Testing and Analysis*, Crystal City, VA, May 26, 2005.

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2. G. Sandrock, K. Gross, and G. Thomas, "Effect of Ti-Catalyst Content on the Reversible Hydrogen Storage Properties of the Sodium Alanates," *J. Alloys Compounds*, 339, 229-308, 2002.
3. S. Lasher, "Comparison of Hydrogen Storage Options," *NHA Annual Hydrogen Conference 2005*, Washington, DC, March 29 – April 1, 2005.
4. R. Ahluwalia, X. Wang, A. Rousseau, and R. Kumar, "Fuel Economy of Hydrogen Fuel Cell Vehicles," *J. Power Sources*, 130, 192-201, 2003.
5. D. Anton, D. Mosher, and S. Opalka, "High Density Hydrogen Storage System Prototype using NaAlH<sub>4</sub> based Complex Compound Hydrides," *FY 2004 Progress Report for the DOE Hydrogen Program*, 230-234, December 2004.
6. P. Benard and R. Chahine, "Modeling of Adsorption Storage of Hydrogen on Activated Carbons," *Int. J. Hydrogen Energy*, 26, 849-855, 2001.