
IV.F.3 System Level Analysis of Hydrogen Storage Options

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Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H₂ storage approaches, to assess and down-select options and to determine the feasibility of meeting DOE targets. Specific objectives in FY 2006 include:

- 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

The Hydrogen, Fuel Cells, and Infrastructure Technologies Multiyear Program Plan technical Storage barriers this project addresses include:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (N) Liquefaction Energy Penalty
- (O) Hydrogen Boil-Off
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (R) Regeneration Processes

Technical Targets

This project is conducting system level analysis to address the DOE 2007 and 2010 technical targets for the on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg in 2007, 2 kWh/kg in 2010
- System volumetric capacity: 1.2 kWh/L in 2007, 1.5 kWh/L in 2010
- Minimum H₂ delivery pressure: 8 atm in 2007, 4 atm in 2010
- Refueling rate: 0.5 kg/min in 2007, 1.67 kg/min in 2010
- Minimum full flow rate of H₂: 0.02 g/s/kW

Accomplishments

- Developed MHtool, an Excel-based analysis tool, to help scientists evaluate how well their metal hydride material, when used in a full-scale device, can meet DOE’s storage targets.
- Determined conditions under which activated carbons at cryogenic temperatures can meet 2007 and 2010 storage targets.
- Determined conditions under which cryo-compressed hydrogen storage can achieve the 2007 targets of 4.5 wt% gravimetric and 36 kg/m³ volumetric capacity.
- Developed FCHtool, an Excel-based analysis tool, to evaluate fuel cycle efficiencies of candidate materials and processes including options that require off-board regeneration of the spent material.
- Led the activities of the Storage Systems Analysis Working Group to foster communication and collaboration across all DOE contractors on system related issues.

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 to meet 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. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and 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 Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects (such as those of TIAX, GTI, and the Centers of Excellence) to assure consistency and to 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 system or internal combustion engine for on-board systems, on-board hydrogen storage subsystem for the off-board systems, etc.).

Results

We developed a computer code - MHtool: Metal-hydride hydrogen storage system analysis tool - and made it available to DOE contractors and the Centers of Excellence (COEs). The scientists can use this tool to (1) evaluate the performance of their material when used in a full-scale device, vis-à-vis DOE's H₂ storage targets, (2) identify specific deficiencies in material properties and their impact on performance of the storage system, and (3) assess how much improvement is needed in the deficient material properties to meet the storage targets.

MHtool is written using the Microsoft Excel platform with embedded macros in visual basic language. The formulation in MHtool is generally applicable to a variety of materials with any hydrogenation and dehydrogenation chemistries. It consists of five modules, MCM, SCM, HTM, SM and DM that run sequentially with the output of one module automatically becoming a part of the input to the next module. MCM is a high-level module that uses experimental data to characterize the storage material for composition and capacity. SCM is a computationally intensive module that calculates the reversible storage capacity of the medium, maximum depth of discharge (DOD) and the maximum state of charge (SOC) subject to the constraints of the minimum delivery pressure of hydrogen, minimum full-flow rate of

hydrogen, refueling time and hydrogen supply pressure. HTM sizes the heat transfer components (number of tubes, tube diameter, tube length, manifolds, etc) for the specified refueling rate, characteristics of the heat transfer fluid, and the enthalpy of hydrogen absorption by the storage medium. SM uses the information from MCM, SCM and HTM modules to determine the size of the enclosure components (liner, carbon fiber, glass fiber and insulation) and hence the gravimetric and volumetric capacity of the system. The last module, DM, calculates the dynamic sorption (charging and discharging) behavior of the metal hydride, taking into consideration the chemical kinetics and heat transfer characteristics.

As an example application of MHtool, Figure 1 presents results from a parametric study conducted using SCM for the NaAlH₄-Na₃AlH₆-NaH system with 4% TiCl₃, 1.6 g/s minimum full flow rate of H₂, 100 bar H₂ supply pressure, 115°C discharge temperature and 165°C peak temperature during refueling. It indicates that the minimum H₂ delivery pressure can affect the recoverable hydrogen storage capacity of the medium. At 0.1 bar back pressure (vacuum), both NaAlH₄ and Na₃AlH₆ can be dehydrogenated; the maximum DOD is about 40% for the Na₃AlH₆ reaction and ~80% for the NaAlH₄ reaction. The second dehydrogenation step cannot be conducted at 8 bar minimum delivery pressure, and the maximum DOD for the first step is only 65%. The result is that the reversible capacity decreases from >2.7% at near vacuum condition to 1.9% at 8 bar back pressure. Similarly, at 8 bar minimum delivery pressure, Figure 1 shows that the recoverable storage capacity decreases from ~1.9% at a H₂ refueling rate of 0.5 kg/min to <1.5% at 2 kg/min. The refueling rate determines the maximum SOC which is calculated to be >98% at 0.5 kg/min but only 67% at 2 kg/min. Figure 1 also shows the effect of discharge kinetics [1] on the maximum DOD. At 8 bar minimum delivery pressure and 0.5 kg/min H₂ refueling rate, a ten-fold enhancement in kinetics is needed to increase the DOD to ~95% from 65% and thereby improve the reversible storage capacity to ~2.8 wt% from 1.9 wt%. With only the first dehydrogenation step active, as at 8 bar back pressure, the theoretical material capacity is ~3.0 wt%.

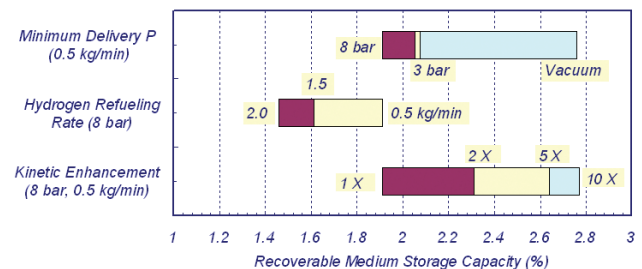


FIGURE 1. Reversible Storage Capacity of Sodium Alanate Medium

Hydrogen Storage on Activated Carbon

In FY 2006, we investigated hydrogen storage in activated carbon (AC) at liquid-N₂ cooled temperatures (77-150 K) and elevated pressures (>100 bar). We reviewed past work in this area and formulated a model to determine hydrogen uptake in the AX-21 activated carbon from the Ono-Kondo theory for adsorption isotherms [2] and hydrogen storage in the void space from the Lee-Kesler equation of state. We assumed that AX-21 in 2 wt% Al-2024 foam 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 MLVSI (10⁻⁵ torr pressure) was determined to limit the heat loss to 1 W and of T700 carbon fiber to provide a 2.25 safety factor at the maximum storage pressure. We assumed that during refueling, liquid-N₂ flows in the tubes of an Al-2024 in-bed heat exchanger to cool the storage medium, liner and carbon fiber.

Figure 3 presents the H₂ storage density of AX-21 medium at 100 K, recoverable density of the AC medium

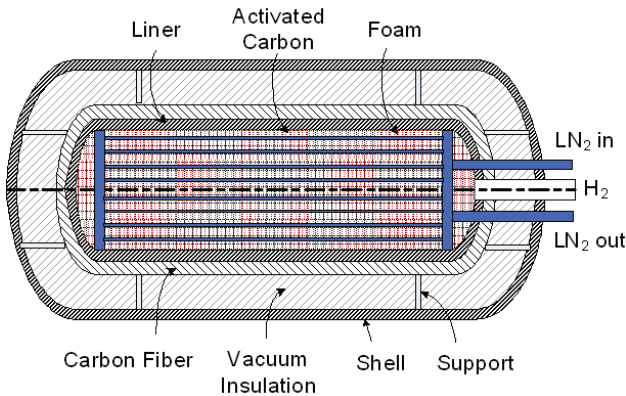


FIGURE 2. Activated Carbon H₂ Storage System

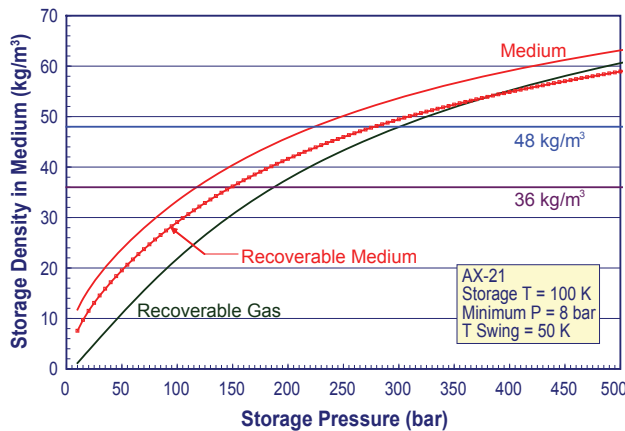


FIGURE 3. Recoverable H₂ Storage Density of AX-21 Medium at 100 K with Temperature Swing

with 50 K temperature swing and 8 bar minimum delivery pressure, and recoverable density of gaseous H₂ under the same conditions. Also included in Figure 3 are the DOE 2007 system target of 36 kg/m³ and the derived medium target assuming 75% volumetric efficiency. Figure 3 shows a breakeven pressure of 380 bar, above which the recoverable storage density is higher for gaseous H₂ and below which it is higher for AX-21 medium. It also shows that a storage pressure of 280 bar is needed to reach the 36 kg/m³ system target using AX-21 which is only marginally lower than the pressure needed with gaseous H₂ alone (no AC). Also, at the breakeven pressure, 16.5% of the recoverable H₂ is stored in the AC and 83.5% is in the void space.

Figure 4 presents the volumetric and gravimetric capacities of the AX-21 storage system (5.6 kg recoverable H₂, 8 bar minimum delivery pressure, 0.5 kg/min H₂ refueling rate) for pressures below the breakeven point. It indicates that a storage pressure >150 bar is needed for the system to meet the 2007 4.5 wt% gravimetric capacity target at 100 K storage temperature and 50 K temperature swing. It also indicates that the volumetric capacity of the system increases with pressure to reach ~35 kg/m³ at 380 bar. It is possible to meet the 36 kg/m³ target by further raising the pressure but for P > 380 bar it is preferable to eliminate the activated carbon and store H₂ purely as compressed gas. Our systems analyses indicate that at 150-380 bar, the volumetric efficiency (i.e., volume of the AC medium divided by the total volume of the system) is 60-62%.

Figure 5 shows the calculated storage capacity of the cryo-compressed hydrogen system (no AC, no temperature swing, 5.6 kg recoverable H₂, 8 bar minimum delivery pressure) at 100 K. We did not include an onboard heat exchanger in this system on the assumption that the storage tank can be charged with compressed H₂ cooled below 100 K. Figure 5 indicates that at pressures above 355 bar, the cryo-compressed

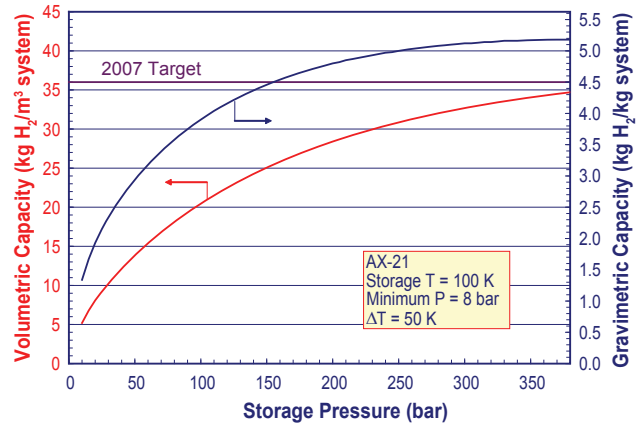


FIGURE 4. Storage Capacity of AX-21 System at 100 K

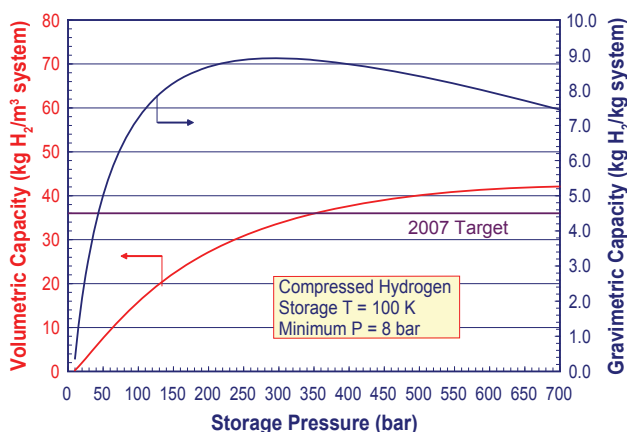


FIGURE 5. Storage Capacity of Cryo-Compressed H₂ System at 100 K

hydrogen storage system may simultaneously meet the 2007 gravimetric and volumetric targets of 4.5 wt% and 36 kg/m³. The system may also meet the 2010 gravimetric target of 6 wt% (2.0 kWh/kg) but not the volumetric target of 45 kg/m³ (1.5 kWh/L). The system has a peak gravimetric capacity of 8.9 wt% at 300 bar. At 355 bar, the minimum pressure at which the 2007 volumetric target is met, the calculated volumetric efficiency is about 70%.

A study was conducted to determine the material H₂ capacities and thermal properties required for a storage system to meet the 2010 targets of 2.0 kWh/kg (6 wt%) and 1.5 kWh/L (45 kg/m³). Based on a preliminary storage system design for a sorbent at 100 K, we concluded that the material H₂ capacity has to be 12-16 wt% and 60±3 g/L in order to meet 2010 system targets for weight, volume, refueling rate and minimum hydrogen delivery pressure. The required gravimetric capacity is 12 wt% if the material thermal conductivity can be enhanced to 5 W/m.K, otherwise a heat transfer support is needed and the required gravimetric capacity is 16 wt%. The material conductivity requirements are set by the 1.5 kg/min H₂ refueling rate.

Fuel Cycle Efficiency of Hydrogen Storage Options

We developed a computer code - FCHtool: Fuel Cycle Efficiency of Hydrogen Storage Options - and made it available to DOE contractors and COE partners. The researchers can use this tool to determine the efficiencies of, and primary energies consumed in, producing, distributing and storing hydrogen with different pathways. The tool runs on the Microsoft Excel platform with embedded macros written in visual basic application language. It can accommodate arbitrary process steps to simulate any hydrogen fuel cycle; it has reference database, which is consistent with GREET [3] and H2A [4], for process fuel production, electricity generation, hydrogen production, hydrogen distribution,

hydrogen storage and hydrogen regeneration; and it outputs primary energy consumption, efficiencies and emissions of regulated pollutants and greenhouse gases.

Figure 6 presents preliminary results from an ongoing FCHtool study on comparing efficiencies of four hydrogen storage options: compressed hydrogen (cH₂), liquefied hydrogen (LH₂), aqueous sodium borohydride (SBH), and MgH₂ slurry. Assumptions were coordinated with the developers of the storage systems and H2A models. For each case, it is assumed that hydrogen is produced at 20 bar and 73% efficiency in a central plant by steam reforming of methane (SMR), with pressure swing adsorption for purification. For the cH₂ option we consider that H₂ is compressed to 68 bar (for pipeline transmission) or 180 bar (for truck delivery) at the production site using a multi-stage compressor, delivered by tube trailers for 1% and pipeline for 50% market share, and recompressed to 125% of the on-board storage pressure at the dispensing site. For the LH₂ option, we consider that H₂ is liquefied at the central production site (7.1 kWh/kg energy consumed in liquefaction, 500,000 tons/day capacity [4]) and delivered by a 400 kg capacity truck in the 1% and 4,000 kg truck in the 50% market scenario. For the MgH₂ slurry option, we assume that the spent Mg(OH)₂ is regenerated by the H₂-assisted low temperature flux - solid oxide membrane process at 1,150°C and that the electricity consumption is 40.7 kWh/kg of H₂ [5]. For the SBH option, we assume that the Brown-Schlesinger process is used in making SBH with NaH and H₃BO₃ coming from the spent sodium metaborate and CH₃OH recycled internally. After Millennium Cell [6], we assume that for every mole of NaBH₄ produced, one mole of sodium is recovered by H₂-assisted electrolysis of NaBO₂ and three moles of sodium are obtained from the H₂-assisted electrolysis of NaOH. Accordingly, the total electricity consumed in the electrolysis steps is 22.4 kWh/kg of H₂. In all cases, we have used the EIA-projected 2015 U.S. grid to define the source of electricity [7].

For the 50% market share scenario, Figure 6a compares the primary energy consumed in producing (SMR), distributing (truck or pipeline) and storing (compression, liquefaction and regeneration) hydrogen in the different storage options. The energy consumed in producing hydrogen for the liquid H₂ option is somewhat higher than for gaseous and chemical hydride options because of an assumed 6.5% boil-off loss. For the compressed gas option, the energy consumed in distributing and storing H₂ is about 17% of the energy consumed in producing H₂ if the storage pressure is 350 bar and 25% if the storage pressure is 700 bar. For the liquid hydrogen option, the storage step consumes about 45% of the energy consumed in producing H₂ and the energy consumed in distributing H₂ is negligible. For the SBH option, the energy consumed in the storage

steps is higher than the energy consumed in producing H_2 . For the MgH_2 slurry option, the storage step needs more than twice the energy consumed in producing H_2 . For these last two cases, the energy consumed in the distribution step is negligible.

Figure 6b compares the efficiencies of the production, distribution and storage steps. As defined, the efficiency of the production step is the same since all five storage options are based on steam methane reforming. The distribution efficiency is 93.5% for the two compressed gas options and >99.5% for the liquefied hydrogen and chemical hydride options. The storage efficiency is 84.3% for 350 bar and 77% for 700 bar cH_2 storage, 58.5% for LH_2 storage, 32.3% for SBH option and 21.1% for the MgH_2 slurry option. The overall well-to-tank efficiency is 58.1% for cH_2 storage at 350 bar, 54.5% for cH_2 storage at 700 bar, 43.9% for LH_2 storage, 28.1% for the SBH option, and 19.2% for the MgH_2 slurry option. The differences in the cycle efficiencies for the different options are mostly due to the varying amounts of energy consumed in storing/regenerating hydrogen.

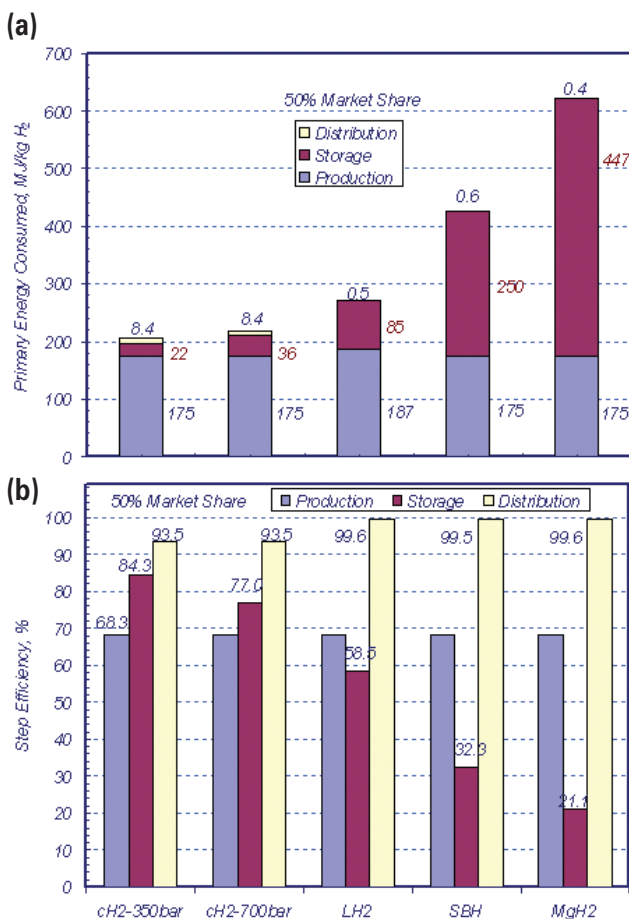


FIGURE 6. Energy Consumption and Efficiencies of Production, Storage and Distribution Steps

Conclusions and Future Directions

- The usable H_2 -storage capacity of a metal hydride is determined not only by the stoichiometry and thermodynamics but also sorption kinetics. It also depends on system parameters and constraints, such as the minimum delivery pressure, refueling rate, minimum full-flow rate of H_2 , and the temperature at which heat is available for dissociating the metal hydride.
- Results to date indicate that commercially available super activated carbon presents only marginal advantages in meeting the 2007 volumetric and gravimetric targets over compressed gas storage.
- Cryo-compressed H_2 at 100 K may simultaneously satisfy the 2007 targets of 1.5 kWh/kg and 1.2 kWh/L at pressures higher than 355 bar. It may also meet the 2010 gravimetric target of 2.0 kWh/kg but does not appear to meet the volumetric target of 1.5 kWh/L.
- A computer code “FCHtool” has been developed and is available for comparing different pathways of producing, delivering and storing H_2 . It is flexible because of the embedded macros that help in evaluating different fuel cycles without restricting the arrangement of the process steps.
- Continue to work with DOE contractors and Centers of Excellence to model and analyze various developmental hydrogen storage systems.
- Expand MHtool to incorporate additional modules, e.g., to deconvolute the pressure-composition-temperature data and to derive kinetic constants from experimental measurements.
- Extend the activated carbon work to other forms of carbon and sorbents.
- Provide independent analysis of the cryo-compressed hydrogen storage option in support of DOE’s go/no-go decision.
- Begin work on developing CHtool for evaluating chemical hydrogen storage materials and systems.

FY 2006 Publications/Presentations

1. R. K. Ahluwalia, “Sodium Alanate Hydrogen Storage System for Automotive Fuel Cells,” Submitted to *International Journal of Hydrogen Energy*, 2005.
2. R. K. Ahluwalia and J-K Peng, “MHtool: Metal-Hydride Hydrogen Storage System Analysis Tool,” DOE Metal Hydride Analysis Kick-Off Meeting, 29 Sept. 2005, Washington, D.C.
3. R. K. Ahluwalia, T. Q. Hua, M. Q. Wang, and R. Kumar, “System Analysis of Chemical Hydrogen Storage Options,” Hydrogen Storage Systems Analysis Working Group Meeting, 12 Oct. 2005, Argonne, IL.

4. R. K. Ahluwalia, J-K Peng and T. Q. Hua, "System Level Considerations for Hydrogen Storage," Storage Systems Analysis Working Group Meeting, 18 Nov. 2005, Palm Springs, CA.
5. R. K. Ahluwalia, J-K Peng and T. Q. Hua, "On-Board Storage Systems Analysis," DOE and FreedomCAR & Fuel Partnership Analysis Workshop, 25 Jan. 2006, Washington, D.C.

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1. G. Sandrock, K. Gross, and G. Thomas, "Effect of Ti-Catalyst Content on the Reversible Hydrogen Storage Properties of the Sodium Aluminates," *J. Alloys Compounds*, 339, 229-308, 2002.
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3. M. Q. Wang, GREET 1.7 – Transportation Fuel-Cycle Model, Argonne National Laboratory, Argonne, IL, December 2005.
4. DOE H2A Analysis, www.hydrogen.energy.gov, December 2005.
5. A. Krishnan, X. G. Liu, and U. B. Pal, "Solid Oxide Membrane Process for Magnesium Production Directly from Magnesium Oxide," *Metallurgical and Materials Transactions B*, 36B, 463-473, 2003.
6. Y. Wu, "Energy Efficiency of Sodium Borohydride Regeneration," DOE Hydrogen Storage Program Analysis Group Meeting, Argonne, IL, October 12, 2005.
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