IV.D.7 Advancement of Systems Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage

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Fiscal Year (FY) 2011 Objectives

- Collaborate closely with the Hydrogen Storage Engineering Center of Excellence (HSECoE) partners to advance materials-based hydrogen storage system technologies.
- Develop vehicle/power plant/storage system integrated system modeling elements to improve specification of storage system requirements and to predict performance for candidate designs.
- Establish detailed heat and mass transfer modeling and apply to design improved internal heat exchange configurations.
- Design and evaluate compacted/structured hydride powder beds including integration into the above heat exchange configurations.
- Assess the viability of on-board purification for various storage material classes and purification approaches.
- Conduct risk assessments during the progression of the phased HSECoE efforts to evaluate concepts regarding the "Environmental Health and Safety" target.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(H) Balance of Plant (BOP) Components
(J) Thermal Management

Technical Targets

The goals of this project mirror those of the HSECoE which by the end of Phase I (March, 2011) seeks to define systems configurations which can fully meet four of the DOE 2010 numerical system storage targets as outlined in the Multi-Year Research, Development and Demonstration Plan (http://www.eere.energy.gov/hydrogenandfuelcells/mypp/) and partially meet the remaining numerical targets to at least 40% of the target or higher.

TABLE 1. Current Status of Four Key System Characteristics

Characteristic	Units	2010 Target	2015 Target	Compacted Material in System	UTRC 2011 Status
System Gravimetric Capacity	kg H_2/kg system	0.045	0.055	SAH	0.0142
				1:1 LAMH	0.0257
System Volumetric Capacity	kg H_2/L system	0.028	0.040	SAH	0.015
				1:1 LAMH	0.018
Efficiency	%	90	90	SAH	70
				1:1 LAMH	75
NH_3 Content	ppm	0.1	0.1	1:1 LAMH or/AB	0.1

SAH - sodium aluminium hydride; LAMH - lithium amide and magnesium hydride; AB - ammonia borane

FY 2011 Accomplishments

Accomplishments of the current project comprise:

- Developed Simulink framework to compare all H_2 storage systems on a common basis.
- Implemented two on-board reversible metal hydride systems in Simulink framework.
- Optimized volumetric capacity and thermal conductivity of two on-board reversible metal hydride materials through compaction and additives.
- Designed compact heat exchanger for SAH pellets that enables a 10.5 minutes refueling time.

- Developed H_2 purification cartridge that enables NH_3 removal down to 0.1 ppm, as required by the SAE J2719 APR2008 guideline.
- Completed qualitative risk assessment of all three H_2 storage system types.
- Demonstrated solid transport of AB surrogate material along a complex path with a flexible screw feeder.
- Evaluated vibration packing of AX-21/MaxSorb in order to increase density of cryo-adsorbent AX-21/MaxSorb but resulting density was only 0.3 g/cm^3 instead of the targeted 0.6 g/cm^3.

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Introduction

Physical storage of hydrogen through compressed gas and cryogenic liquid approaches is well established, but has drawbacks regarding weight, volume, cost and efficiency which motivate the development of alternative, materials-based methods of hydrogen storage. Recent worldwide research efforts for improved storage materials have produced novel candidates and continue in the pursuit of materials with overall viability. While the characteristics of the storage materials are of primary importance, the additional system components required for the materials to function as desired can have a significant impact on the overall performance. Definition, analysis and improvement of such systems components and architectures, both for specific materials and for generalized material classes, are important technical elements to advance in the development of superior methods of hydrogen storage.

Approach

UTRC's approach is to leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials-based H_2 storage for automotive applications. UTRC focused in the second year of the HSECoE project on screening H_2 storage system improvement ideas resulting from compaction, thermal conductivity enhancement, H_2 purification, compact and low weight heat exchanger design and system integration. Results contributed to the selection of storage systems that were more likely to meet DOE targets when further developed in Phase 2 during the Phase 1 to Phase 2 go/no-go meeting.

Results

Complex metal hydrides like Ti-doped SAH and mixtures of LAMH offer a higher gravimetric hydrogen storage capacity (e.g. SAH: 3.2 wt% H_2; 1:1 LAMH: 8.2 wt%) than interstitial metal hydrides (e.g. $Ti_{1.1}CrMn$: 1.7 wt% H_2) but have a relative low density which affects their volumetric capacity. Applying these materials in

powder form further reduces their volumetric capacity to levels below the 2015 volumetric capacity target (40 g H_2/L of system). It is therefore important to consider powder compaction.

The effect of powder compaction on the thermal conductivity of SAH was reported in the previous annual report and efforts in the second year focused on improving the thermal conductivity of SAH to 5-8 W/m/K by using additives. UTRC selected aluminum powder and expanded natural graphite (ENG). The results show that the effective thermal conductivity of the SAH/aluminum mixtures follows the series model for thermal conductivity which makes aluminum powder fairly ineffective in improving the thermal conductivity of SAH as a large aluminum volume fraction would be required [1]. It is better to apply aluminum in the form of fins in a fin and tube heat exchanger as an effective thermal conductivity of 4 W/m/K can be achieved with only 4 volume percent of aluminum and compacted SAH pellets. The effective thermal conductivity of SAH with expanded natural graphite followed the parallel model for thermal conductivity [1], which enabled high values of the thermal conductivity at a relatively low volume fraction of this additive. Best results were obtained when using ENG 'worms', kindly provided by SGL Carbon, that introduce thermal conductivity anisotropy upon uniaxial compaction with the highest value of the thermal conductivity perpendicular to the pressing direction and in the direction of the heat exchanger tube. A COMSOL model was developed in order to extract information about the thermal conductivity anisotropy from the thermal conductivity measurements. Heat exchanger tubes no longer require fins when using compacted SAH pellets with about 5 wt% ENG 'worms' to improve the thermal conductivity.

UTRC applied compaction know-how of SAH to the LAMH material in this second year of the HSECoE project. The LAMH material was much more difficult to compact than SAH and required the addition of expanded natural graphite binder in order to obtain samples with a sufficient strength. Thermal conductivity measurements showed that LAMH required a larger weight fraction of ENG 'worms' (e.g. 15 wt%) than SAH (e.g. 5 wt%) in order to obtain high thermal conductivity values in the direction of the heat exchanger tube that would allow a rapid refueling process when it would be possible to substantially improve the slow H_2 absorption kinetics and reversibility of the current LAMH material.

Kinetic measurements from Ti-doped SAH powders and pellets were analyzed in order to obtain values of the model parameters in the kinetic expressions that are used in the detailed COMSOL Multiphysics™ model [2,3], which was developed in the first year of the HSECoE project for obtaining a better understanding about the impact of thermal gradients during refueling upon the H_2 absorption rate. Results showed that one set of model parameters can be used for SAH in its powder and compacted form. The detailed COMSOL model was modified accordingly

and experimentally determined values of densities and thermal conductivities of SAH (without ENG 'worms') were implemented in order to optimize the heat exchanger configuration for a fast refueling time. The results are shown in Figure 1. Small diameter aluminum tubing with aluminum fins are projected to provide sufficient heat transfer in order to reach 90% of the materials H_2 storage gravimetric capacity in about 10.5 minutes, which was the maximum allowable refueling time for the Phase 1 to Phase 2 Go/No-Go decision. A faster refueling time will require materials development in order to improve the reaction kinetics and it will require an increase in the aluminum volume fraction of the heat exchanger in the metal hydride tank. Figure 1 clearly shows the benefit of compaction on the volumetric capacity of the SAH bed. Uncertainty about the heat transfer coefficient between the SAH pellet and the heat exchanger tube has driven the development of an experimental test apparatus which will be used to study H_2 absorption and heat transfer by SAH pellets stacked around a heat exchanger tube in Phase 2.

The H_2 storage system is expected to experience 1,500 cycles over its lifetime. A series of tests was performed in order to study the effect of H_2 absorption and desorption cycles on the strength of SAH pellets. SAH pellets with aluminum mesh reinforcement (Figure 2) have a higher strength than unreinforced SAH pellets but the strength of both types of pellets rapidly degrades upon cycling due to a substantial expansion of the SAH pellets.

UTRC leads the Integrated Power Plant Storage System Modeling technical area, which fostered a successful collaboration between the HSECoE partners. This resulted in a Simulink framework [4] that includes a vehicle level module (National Renewable Energy Laboratory), a fuel
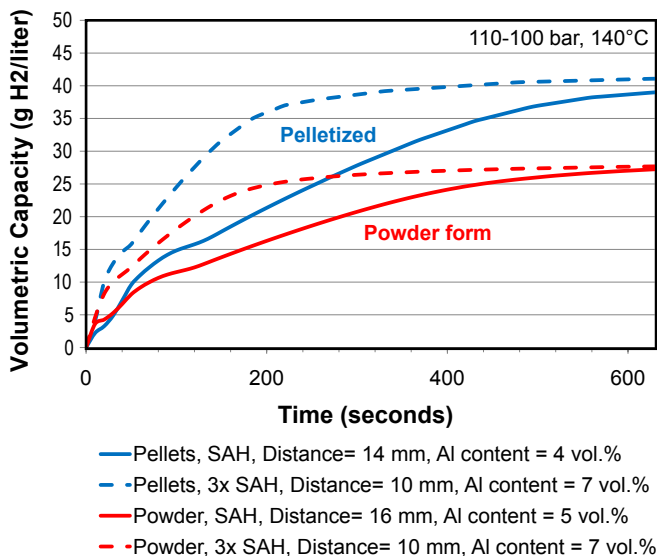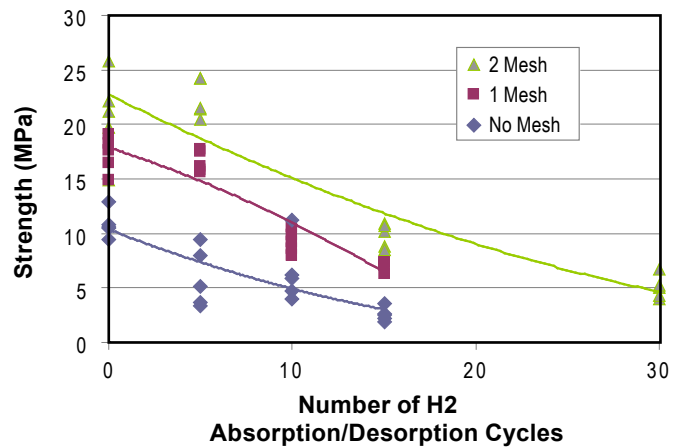
FIGURE 2. Effect of H_2 absorption and desorption cycles on the biaxial flexure strength of SAH pellets with and without internal mesh reinforcement.

cell module (Ford) and various representations of H_2 storage systems as formulated by General Motors (GM), UTRC, Jet Propulsion Laboratory, Savannah River National Laboratory, and the Pacific Northwest National Laboratory (PNNL), as shown in Figure 3. The framework is used within the HSECoE to compare all H_2 storage systems on a common basis. UTRC developed and implemented system models with SAH and LAMH in their powder or compacted form and 350 bar and 700 bar compressed H_2 gas benchmark systems in the Simulink framework. The LAMH system assumed similar heat transfer characteristics as the SAH system. Both systems operate at temperatures that are substantially higher than the temperature at which waste heat from the proton exchange membrane fuel cell can be made available and therefore require H_2 combustion in order to generate heat for hydrogen desorption during a drive cycle. H_2 combustion is also required to heat the storage systems to their operating temperature during a cold start. Such H_2 needs to be readily available and will hence need to be stored in the free volume of the tank or in a separate buffer volume. It was discovered from system simulations that the tank with compacted SAH pellets would no longer contain sufficient H_2 for a cold start and that therefore an additional buffer volume had to be made available to the system. This additional buffer volume reduces the benefits from powder compaction but the H_2 storage tank with the compacted material still occupies a smaller volume than a similar system with the material in its powder form. It is now being studied how the buffer volume can be reduced in order to improve the system volumetric capacity.

Balance of plant (BOP) components were selected by GM and PNNL and information about the weight of the carbon composite type IV pressure vessel were obtained from Lincoln Composites. This information was used to calculate the gravimetric and volumetric capacity of these two metal hydride H_2 storage systems and the results are shown in Figure 4, and also reported in Table 1. The
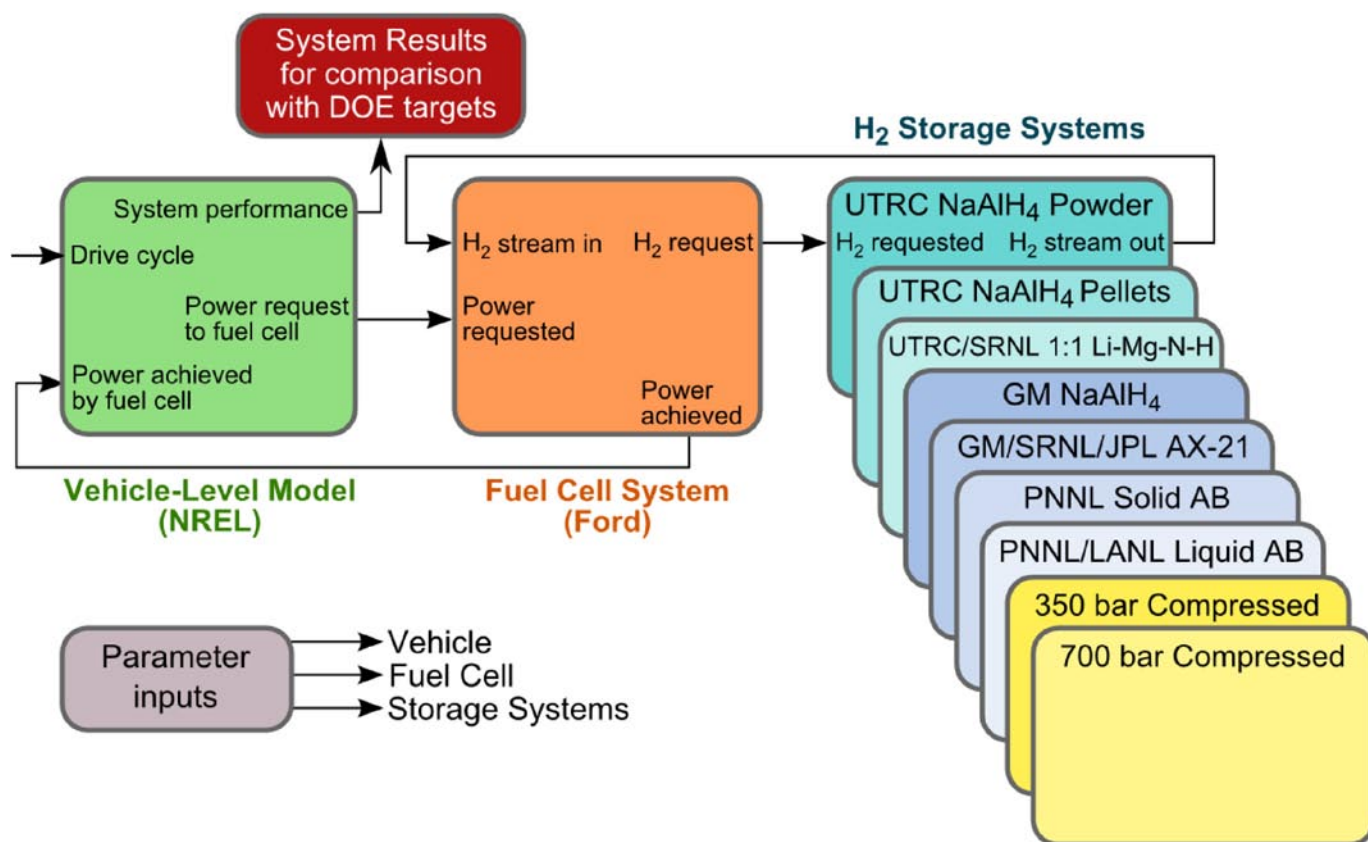
FIGURE 1. Volumetric capacity of the SAH bed, including the aluminum fin and tube heat exchanger, optimized for a 10.5-minute refueling time with SAH in powder or compacted form.

FIGURE 3. Simulink Framework for Comparing all H_2 Storage Systems on a Common Basis
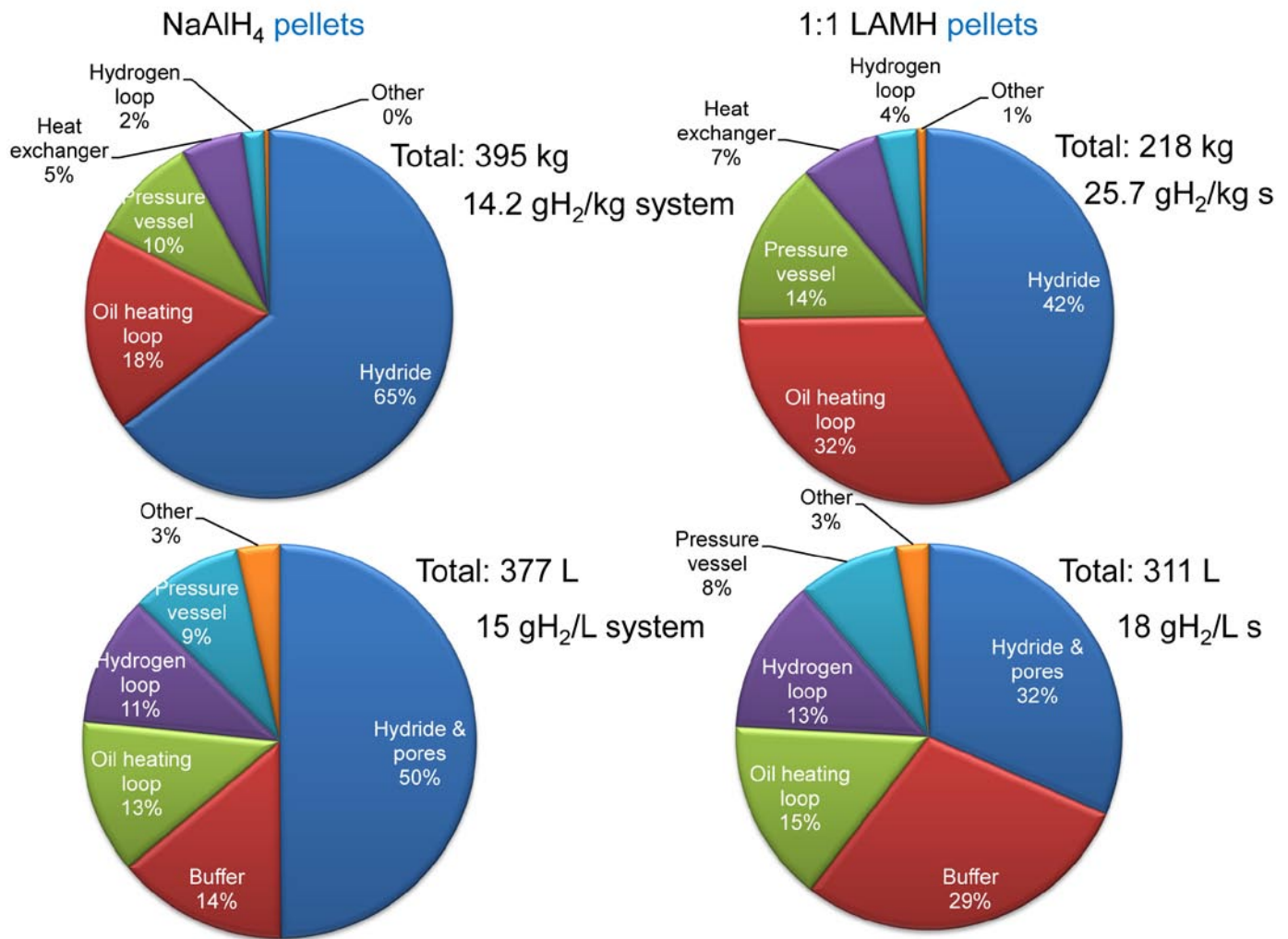
gravimetric capacity of both systems is below the 2010 target and so is their volumetric capacity. It is therefore concluded that the on-board reversible metal hydride systems considered during Phase 1 of the HSECoE are heavy and occupy a much larger volume than the DOE targets allow. This is partly driven by the relative high weight and volume of the BOP components. This gets aggravated when using the heavy BOP components in combination with metal hydride materials like LAMH that have a higher materials gravimetric capacity. Reducing the BOP weight and volume is therefore critical when developing on-board reversible metal hydride H_2 storage systems that require supplementary heating by means of H_2 combustion.

All three H_2 storage systems in the HSECoE have issues related to H_2 quality [5] that need to be addressed. Particulate filters have been recommended by two suppliers in order to contain the cryo adsorbent and on-board reversible metal hydride materials within the pressure vessel while meeting the SAE J2719 APR2008 H_2 purity guideline (particulate size: <10 µm; particulate concentration: <1 µg/l). The standard test method ASTM D7650 standard was identified for assessing the presence of particulates in hydrogen released by the storage systems. UTRC characterized chemical and physical adsorbents for removing NH_3 from hydrogen that is released by the chemical hydride AB and the metal hydride LAMH. Most of the sorbents had

a NH_3 dynamic sorption capacity of about 2 wt%. It was shown that the physical adsorbent Selexsorb CD™ (BASF) has the advantage that is can be regenerated without loss of capacity. Cu-BTC metal organic framework was shown to have a very high NH_3 dynamic sorption capacity (12 wt%) but unfortunately it was very expensive and experiments showed that it could not be regenerated after NH_3 exposure.

UTRC performed qualitative risk assessments of all three H_2 storage systems with the objective to identify the critical risks, failure modes and other technical challenges. One critical risk for a sodium alanate H_2 storage system is dust explosion in air caused by an accidental rupture of the storage vessel upon collision. An example of a critical risk for an AB-based chemical hydride system is a runaway chemical reaction resulting from a loss of the exothermic heat removal capability in the system. Loss of vacuum insulation is a critical risk for the cryo-adsorbent system. It has been suggested to develop a framework for safety categorization of H_2 storage materials for on-board vehicular applications as the risks associated with the various materials vary widely.

Brainstorming resulted in several concepts that could be used to transport chemical hydrides like AB in their solid form on board a vehicle. The flexible screw feeder concept was selected for an experimental evaluation. The system was designed and constructed from off the shelve components

FIGURE 4. Effect of BOP Components on the Gravimetric and Volumetric Capacity of H_2 Storage Systems using SAH or LAMH

and is shown in Figure 5 with the flexible screw transporting an AB surrogate material in a powder form at high rate along a complex path with a 180 degrees bend. Tests were performed to quantify solid transport rate as a function of the flexible screw pitch, rotational speed and bend angle. Solid transport was rejected as a viable technology after PNNL experienced practical problems with transporting AB powder through a heated zone by means of an auger.

Conclusions and Future Directions

Conclusions derived from the work in FY 2011 are:

- ENG 'worms' are effective additives that increase the thermal conductivity of (complex) metal hydride materials and can serve as a binder for materials like LAMH mixtures.
- SAH pellets with and without internal mesh reinforcement show a rapid decline of their strength

upon H_2 absorption and desorption cycles due to volumetric expansion of the SAH phase.

- The current generation of BOP components is heavy and occupies a large volume, which negatively impacts the gravimetric and volumetric capacity that can be achieved with the complex metal hydrides considered during Phase 1 of the HSECoE.
- Complex metal hydrides that require supplemental heating need a substantial H_2 buffer volume in order to enable a cold start during which the system is heated to its operating temperature.
- Several sorbents have been identified that can capture NH_3 emissions from materials based H_2 storage systems based on AB and LAMH in order to improve H_2 quality.

Future work will comprise:

- Explore binderless compaction of AX21/MaxSorb.
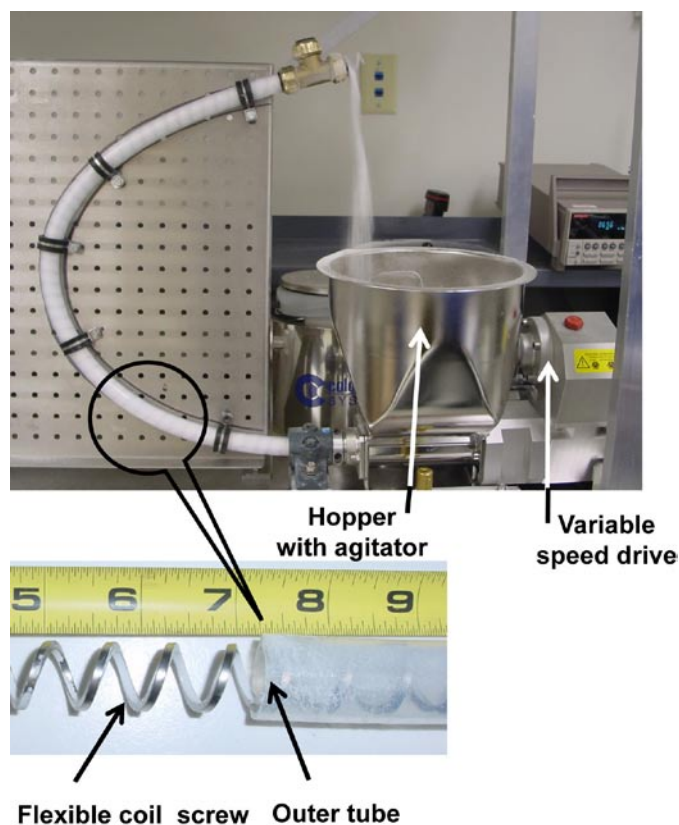
FIGURE 5. Solid Transport of a Surrogate Material with a Flexible Screw along a Complex Path

- Identify ideal material properties of on-board reversible metal hydride material that will enable H_2 storage systems that meet all DOE targets.
- Sensitivity studies with Simulink framework in order to optimize system design.
- Improve understanding of repeated cold starts on system performance.
- Engineering of specialty components for H_2 storage systems and their experimental evaluation.
- Experimental evaluation of purification cartridge connected to H_2 generated from the thermolysis of liquid AB.
- Particulate mitigation strategy evaluation.
- Design failure modes and effects analysis of H_2 storage systems.
- Improve understanding of Department of Transportation requirements for materials-based H_2 storage systems.

FY 2011 Publications/Presentations

1. B.A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, B. Laube and L. Pryor, Engineering Improvement of NaAlH$_4$ System, AIChE Topical Conference: Hydrogen Production and Storage: Hydrogen Storage System Engineering and Applications, November 7–12, 2010, Salt Lake City, UT, USA, to be published in the Int. J. Hydrogen Energy.

2. José Miguel Pasini, Bart A. van Hassel, Daniel A. Mosher and Michael J. Veenstra, System modeling methodology and analyses for materials-based hydrogen storage, AIChE Topical Conference: Hydrogen Production and Storage: Hydrogen Storage System Engineering and Applications, November 7–12, 2010, Salt Lake City, UT, USA, to be published in the Int. J. Hydrogen Energy.

3. Bart A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, B. Laube, L. Pryor, Fanping Sun, Igor Fedchenia and A.E. Kuczek, Engineering progress in materials based H$_2$ storage for light-duty vehicles, IEA HIA Task 22, Fremantle, WA, Australia, January 16–20, 2011.

4. Bart A. van Hassel, J.M. Pasini, D. Mosher, M. Gorbounov, J. Holowczak, I. Fedchenia, J. Khalil, F. Sun, X. Tang, R. Brown, B. Laube and L. Pryor, Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage, Annual Merit Review, Crystal City, Virginia, May 11, 2011.

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1. B.A. van Hassel, D. Mosher, J.M. Pasini, M. Gorbounov, J. Holowczak, X. Tang, R. Brown, B. Laube and L. Pryor, Engineering Improvement of NaAlH$_4$ System, AIChE Topical Conference: Hydrogen Production and Storage: Hydrogen Storage System Engineering and Applications, November 7–12, 2010, Salt Lake City, UT, USA, to be published in the Int. J. Hydrogen Energy.

2. Bruce J. Hardy and Donald L. Anton, Hierarchical methodology for modeling hydrogen storage systems. Part I: Scoping models, International Journal of Hydrogen Energy 34 (2009), pp. 2269-2277.

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5. Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles, SAE International Surface Vehicle Information Report, J2719 APR2008, Revised 2008-04.