

## IV.B.3 Advancement of Systems Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage

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- Assess the viability of onboard purification for various storage material classes and purification approaches.
- Conduct risk assessments during the progression of the phased HSECoE efforts.
- Collaborate closely with HSECoE partners to advance materials-based hydrogen storage system technologies.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.5) of the Fuel Cell Technologies Office 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 to advance hydrogen storage system technologies toward the DOE Hydrogen Program's 2017 storage targets in Table 1 [1].

**TABLE 1.** Status of UTRC's S\*M\*A\*R\*T Milestones

Characteristic	Units	S*M*A*R*T Targets	Storage System Type	UTRC 2013 Status
Gas/Liquid Separator	kg	<5.4	Chemical Hydrogen Storage System	5.8
	L	<19		2.7
	ppm	<100		800±200
Ammonia Filter	kg	<1.2	Chemical Hydrogen Storage System	1.1
	L	<1.6		1.6

### Overall Objectives

UTRC's overall objectives mirror those of the Hydrogen Storage Engineering Center of Excellence (HSECoE) to advance hydrogen storage system technologies toward the DOE Hydrogen Program's 2017 storage targets. Outcomes of this project will include:

- A more detailed understanding of storage system requirements.
- Development of higher performance and enabling technologies such as novel approaches to heat exchange, onboard purification and compacted storage material structures.
- Component/system design optimization for prototype demonstration.

### Fiscal Year (FY) 2013 Objectives

- Develop vehicle/powerplant/storage system integrated system modeling elements to improve specification of storage system requirements and to predict performance for candidate designs.
- Engineer and test specialty components for H<sub>2</sub> storage systems.

### FY 2013 Accomplishments

Accomplishments during the current project period comprise:

- Developed the architecture of a graphical user interface (GUI) for the Simulink framework. Obtained feedback through a beta-test with Sandia National Laboratories (SNL), Oak Ridge National Laboratory (ORNL) and the National Renewable Energy Laboratory (NREL).
- Built gas/liquid separator (GLS) test facility for chemical hydrogen storage system.

- Collaborated with vendor on the design of an axial GLS with a low profile that is capable of meeting the S\*M\*A\*R\*T milestone targets.
- Quantified the performance of the GLS as a function of flow rate, pressure, and temperature.
- Developed computational fluid dynamics (CFD) model of the GLS and modified experimental setup to validate the model by measuring the droplet size distribution in the outlet of the GLS.
- Optimized MnCl<sub>2</sub> loading on super-activated carbon (SAC) IRH-33 for a high capacity and regenerable NH<sub>3</sub> sorbent material in order to minimize weight, volume, and pressure drop of the filter in the chemical hydrogen storage system.
- Delivered optimized filter to Los Alamos National Laboratory (LANL) for competitive adsorption assessment with borazine. Fuel cell grade H<sub>2</sub> was demonstrated with the combined filter assembly.
- Performed qualitative risk analysis of HSECoE designs/materials by performing flammability tests of ammonia borane (AB) in powder and slurry form and by developing a metal-organic framework (MOF)-5 dust explosion test plan for Ford/BASF.



## 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 and cost. 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<sub>2</sub> storage for automotive applications. During the fourth year of the HSECoE project, UTRC continued the development of the Simulink framework for comparing H<sub>2</sub>

storage systems on a common basis. A GUI was developed in order to facilitate the use of this Simulink framework by a wider audience. UTRC downsized a GLS design to the scale that is required for an automotive application of the chemical hydrogen storage system. UTRC built an experimental test facility for testing this GLS and validated the design concept by demonstrating the S\*M\*A\*R\*T milestone. UTRC developed a CFD model of the GLS and performed test facility modifications in order to enable model validation. UTRC's approach to H<sub>2</sub> purity for the chemical hydrogen storage system was to optimize the composition of the NH<sub>3</sub> sorbent material in order to minimize weight, volume and pressure drop while demonstrating the SAE International (SAE) purity target [2]. UTRC developed and validated a dynamic breakthrough model of the NH<sub>3</sub> sorbent bed. UTRC's approach to H<sub>2</sub> purity for the cryo-adsorption system was to evaluate different types of particulate filters.

## RESULTS

UTRC designed the architecture of a GUI of the Simulink framework in which different H<sub>2</sub> storage systems are compared on a common basis, as illustrated in Figure 1. The GUI was subsequently beta-tested with SNL, ORNL and NREL in order to obtain valuable feedback before making it available on the HSECoE website.

Safety and risk assessment has a central place in all the work that is performed at UTRC and within the HSECoE. UTRC developed a MOF-5 dust explosion test plan for Ford/BASF, and the initial results were reported by Ford/BASF at the tech team review in March 2013 and during the 2013 Annual Merit Review. UTRC assessed the ignition properties of AB as slurry in silicone oil and as a powder. The results of these tests are shown in Figure 2. The ignition properties of AB were similar in both tests. However, ignition of H<sub>2</sub> (generated during the exothermic AB thermolysis) can ignite the silicone oil slurring agent while in air.

UTRC optimized an ammonia sorbent for the chemical hydrogen storage system in collaboration with the Université du Québec à Trois-Rivières, Canada. The sorbent makes it possible to scrub NH<sub>3</sub> down to 0.1 ppm with a replacement/regeneration interval of 1,800 miles of driving at an inlet NH<sub>3</sub> concentration of 500 ppm while having a mass and volume of 1.2 kg and 1.6 liters, respectively, which is an important S\*M\*A\*R\*T milestone for the chemical hydrogen storage system development within the HSECoE. The results of the optimization study are shown in Figure 3. Fifty wt% MnCl<sub>2</sub> on SAC IRH-33 resulted in the most compact filter. This also resulted in a full-size filter with the lowest pressure drop, as shown in Figure 4. The dynamic breakthrough capacity of UTRC's sorbent filter was shown to be a factor of 6 higher than commercially available NH<sub>3</sub> sorbent materials. UTRC's NH<sub>3</sub> sorbent is regenerable, as discussed in the previous annual report [3]. UTRC characterized the sorbent material

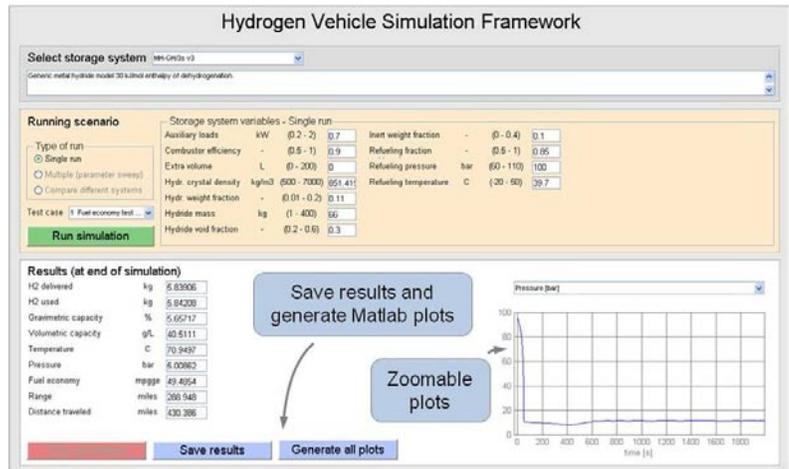
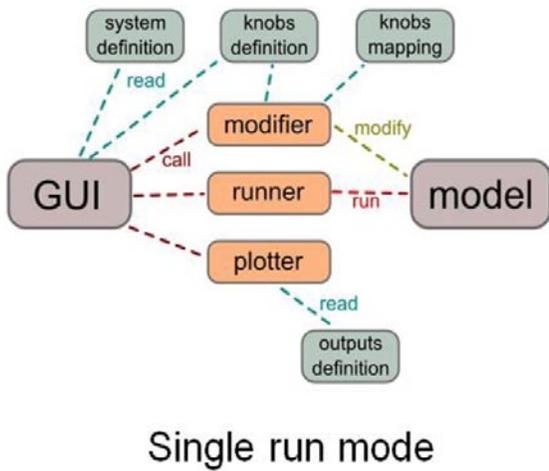


FIGURE 1. Architecture of GUI for Simulink framework.

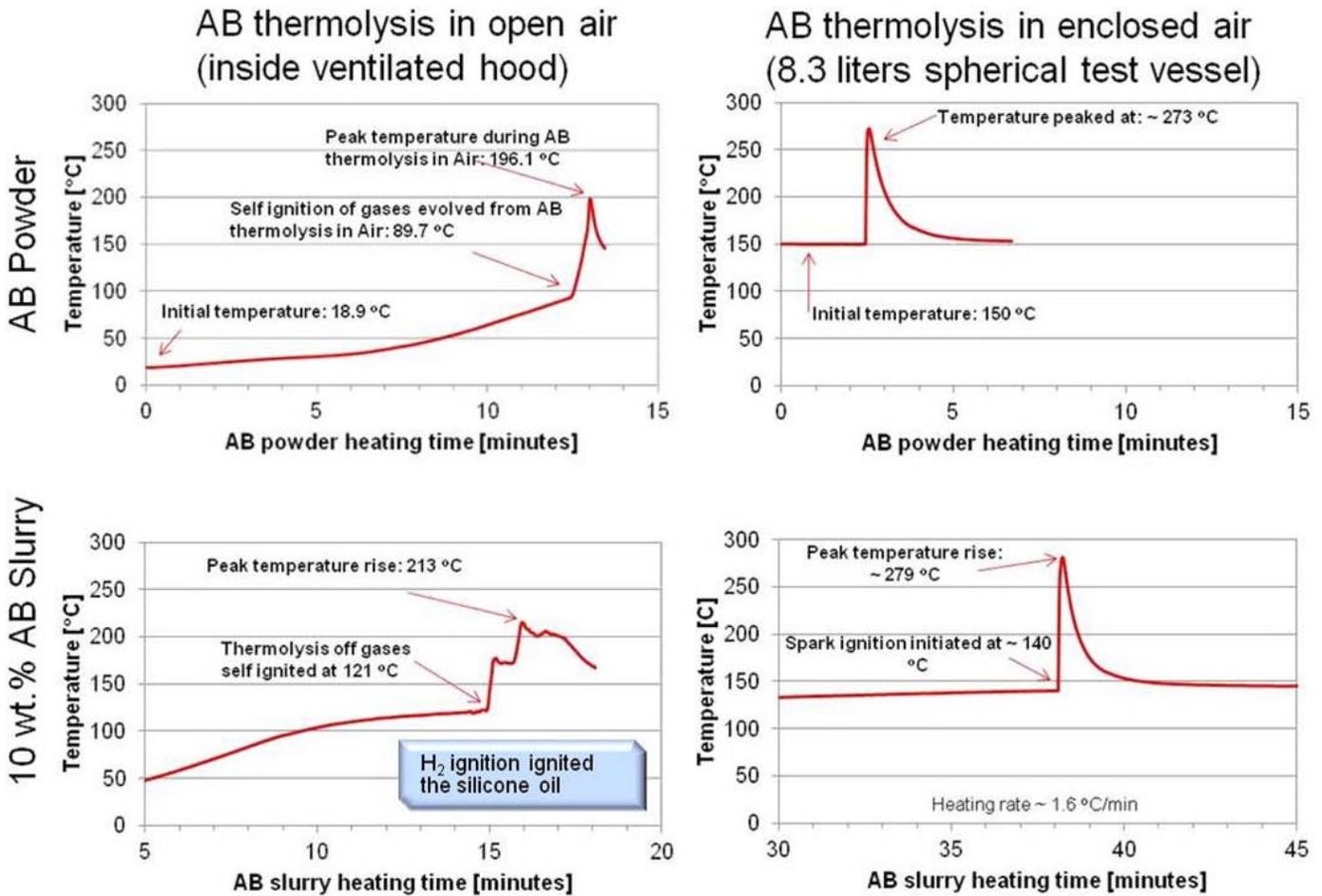


FIGURE 2. Comparison of ignition properties of AB in a silicone oil slurry and in powder form. One series of experiments was performed in open air while a second series of experiments was performed in a closed vessel.

by measuring the  $NH_3$  adsorption isotherm over a wide range of temperature, as shown in Figure 5. A model was developed in order to explain the shape of the adsorption isotherm [4].

The isotherm data were used as input to a COMSOL model of the dynamic impurity breakthrough of a sorbent bed [5]. The model is getting validated with dynamic sorption capacity

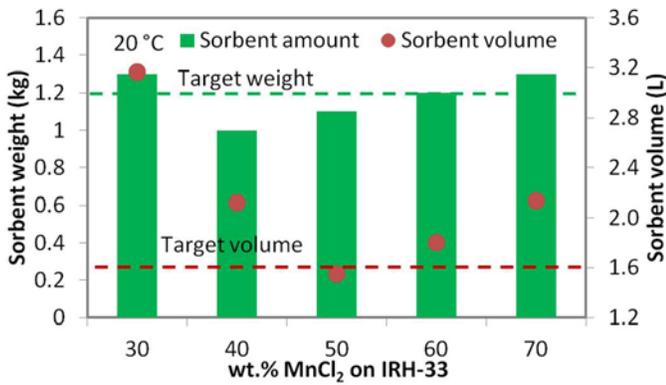


FIGURE 3. Optimization of MnCl<sub>2</sub> loading on SAC IRH-33 for NH<sub>3</sub> filter.

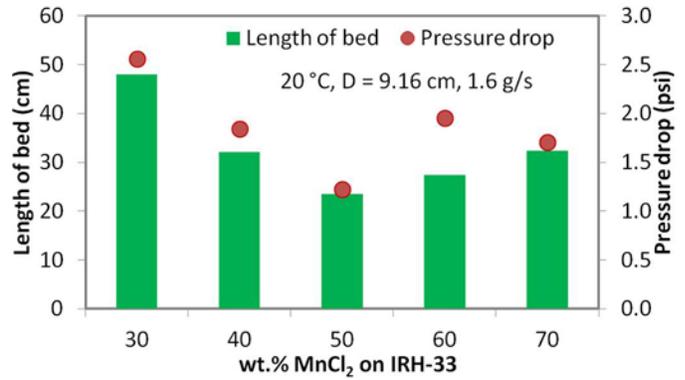


FIGURE 4. Bed length and pressure drop of NH<sub>3</sub> filter.

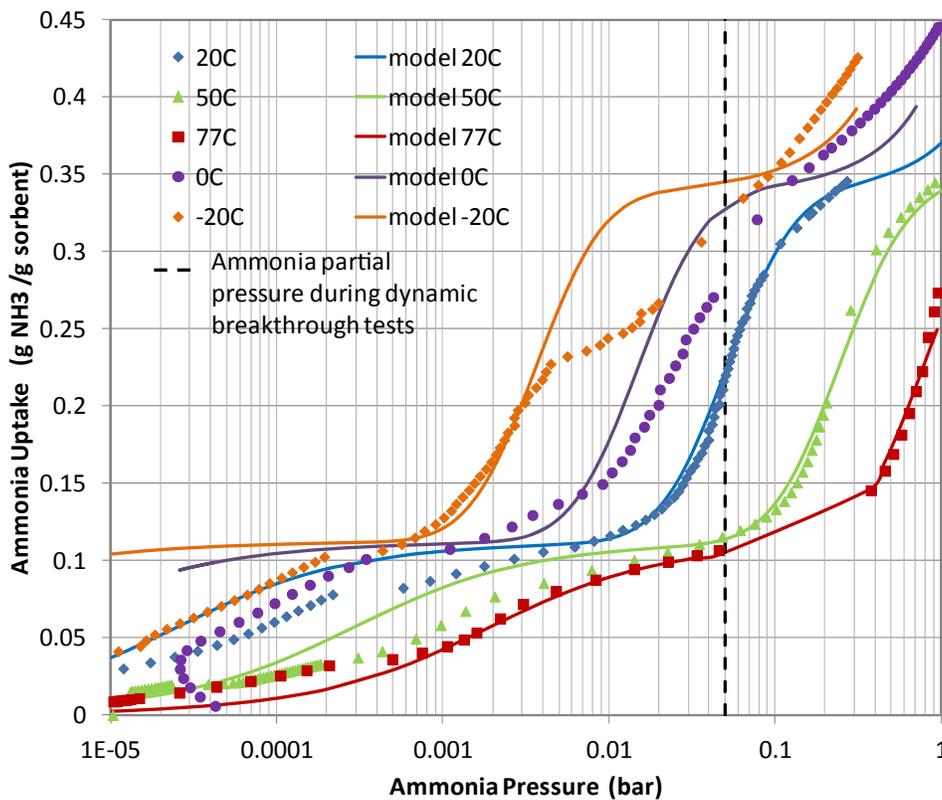


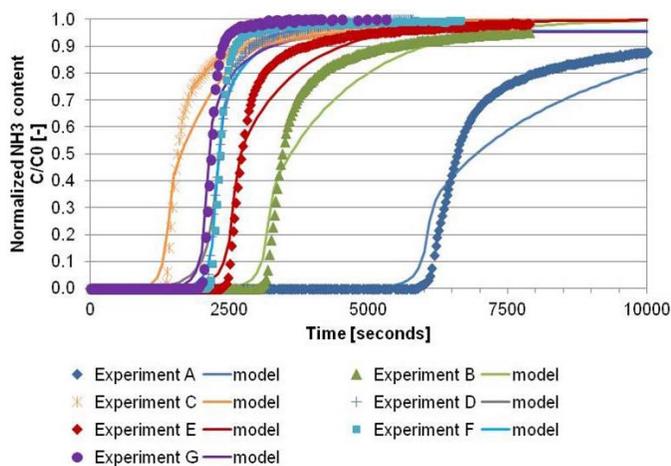
FIGURE 5. NH<sub>3</sub> adsorption isotherms of 40 wt% MnCl<sub>2</sub> on SAC IRH-33.

data as a function of flow rate, pressure and temperature and some initial results are shown in Figure 6.

H<sub>2</sub> quality from cryo-adsorption systems is impacted by particulates that get entrained into the hydrogen that is supplied to the fuel cell system. UTRC evaluated the performance of porous metal particulate filters to mitigate particulates and for containing the adsorbent material in its storage tank. The particulate concentration was measured by means of an engine exhaust particle sizer spectrometer downstream of a particulate filter in a packed bed of Maxsorb\* and MOF-5 powder at room temperature.

Measurements at high flow rates showed the formation of a filter cake and a corresponding increase in pressure drop. The results indicate that a 0.5 micrometer porous metal filter is capable of reducing the particulate concentration to a level of 400 µg/m<sup>3</sup>, which is below the SAE J2719 guideline [3] of 1,000 µg/m<sup>3</sup>. Filter type and size need to be carefully selected for cryogenic and flow-through cooling operating conditions.

A fluid-based chemical hydrogen storage system, such as for instance AB dissolved in ionic liquids (as being developed by LANL) or suspended in a slurry (as being developed by the Pacific Northwest National Laboratory, PNNL),

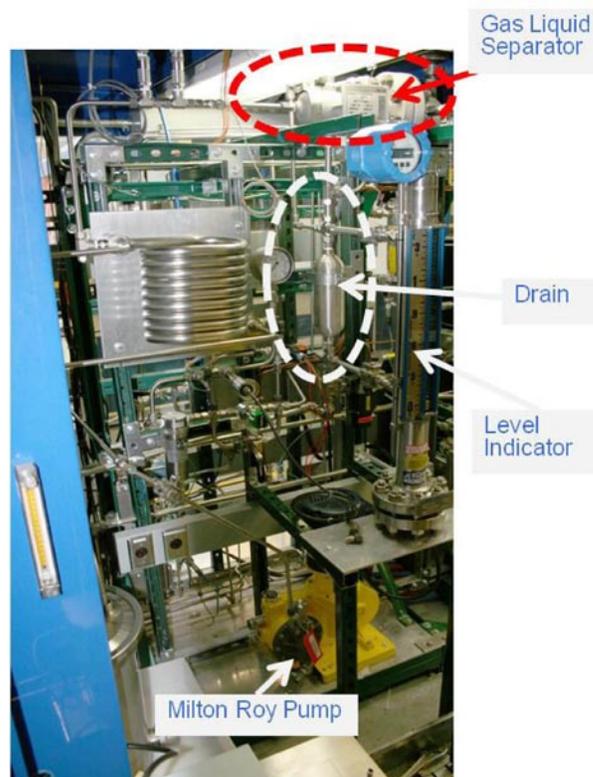


**FIGURE 6.** Dynamic breakthrough modeling of NH<sub>3</sub> through a filter with 40 wt% MnCl<sub>2</sub> on IRH-33 under various operating conditions (flow rate, pressure and temperature).

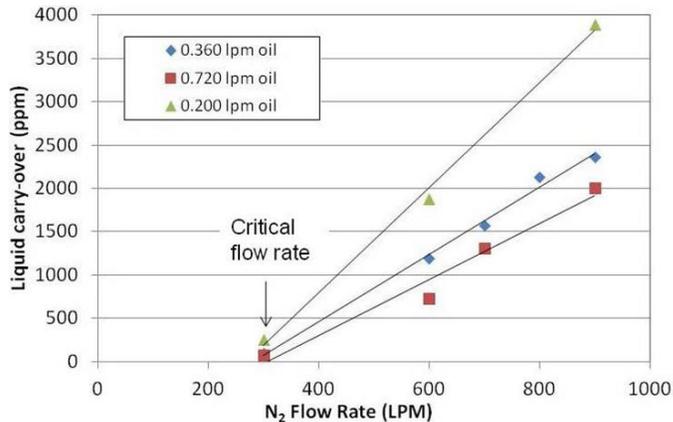
requires a GLS. It separates hydrogen gas produced during AB thermolysis from the fluid that will also contain the AB thermolysis byproducts (e.g. BNH<sub>x</sub>). UTRC collaborated with a vendor on downsizing a passive GLS design with a low profile and no moving parts that deploys three different separation mechanisms: coalescence, gravity and centrifugal action. UTRC built a GLS facility for testing the GLS performance under the S\*M\*A\*R\*T milestone conditions, as shown in Figure 7. The key components were discussed in the previous quarterly report [2].

UTRC quantified the performance of the GLS with a three-factor two-level factorial design of experiment with the following factors: 1) gas and liquid flow rate N<sub>2</sub>: 300 slpm (oil: 360 ml/min) and N<sub>2</sub>: 600 slpm (oil: 720 ml/min); 2) pressure (6 and 12 bar); and 3) temperature (70 and 170°C). N<sub>2</sub> gas was used instead of H<sub>2</sub> gas and the liquid phase was silicone oil AR-20 (viscosity: 20 mPa·s at 25°C), as used by PNNL and LANL in their AB slurries. The temperature was shown to have a large effect on the efficiency of the gas/liquid separator, prompting the need to cool down the two-phase mixture before separation when such a silicone oil would be used as a slurring agent. UTRC demonstrated that the silicone oil could be separated from N<sub>2</sub> gas with a 99.99% efficiency (100 ppm carry-over) at 70°C and 12 bar (abs) pressure under reduced flow conditions (i.e. 360-720 ml/min of liquid phase and 300 slpm of N<sub>2</sub> gas instead of 720 mL/min liquid phase and 600 slpm of N<sub>2</sub> gas for the S\*M\*A\*R\*T milestone), as shown in Figure 8. The experimental results clearly show a critical N<sub>2</sub> gas flow rate above which the liquid carry-over starts to increase. The GLS had a mass and volume of 5.8 kg and 2.7 liters, respectively, which was slightly above the 5.4 kg weight target but well below the 19 liters volume target.

An axi-symmetric CFD model was developed of the GLS. The model predicts that droplets smaller than

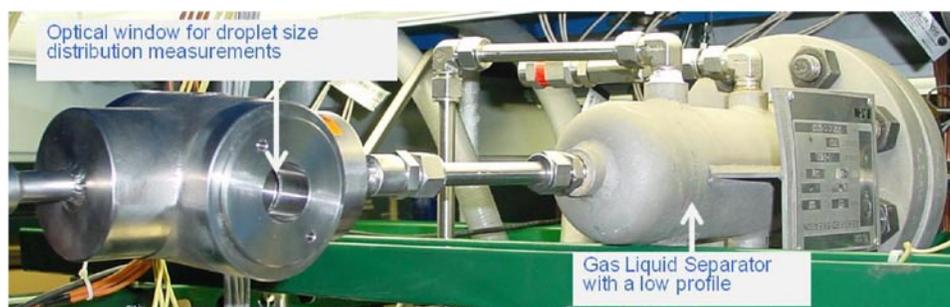


**FIGURE 7.** GLS test facility at UTRC.



**FIGURE 8.** Liquid carry-over results of GLS at 12 bar and 70°C. The liquid carry-over in ppm is defined as the ratio of the silicone oil mass that was separated out of the N<sub>2</sub> gas by a coalescence filter downstream of the GLS and the silicone oil mass that was co-injected with N<sub>2</sub> at the inlet of the GLS.

50 micrometers cannot be separated as these tiny droplets will simply follow the streamlines of the gas and carryover into the vortex finder and out of the GLS. Two phase flow correlations were used to determine design parameters that can be used for minimizing the formation of such small droplets. An optical high-pressure side glass assembly was installed downstream of the GLS in order to measure the outlet droplet size distribution in support of model validation,



**FIGURE 9.** Side-glass assembly for droplet size distribution measurements at outlet of GLS.

as shown in Figure 9. Such measurements will be part of the orderly completion of the chemical hydrogen storage system development work in calendar year 2013, as the DOE elected to discontinue the chemical hydrogen storage system development at the end of Phase 2 of the HSECoE project.

## CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2013 are:

- The Simulink framework is critical for comparing the performance of different H<sub>2</sub> storage systems on a common basis and can be made more user-friendly through the development of a graphical user interface.
- AB as a slurry in silicone oil has similar ignition properties as AB in powder-form but the silicone oil acts as an additional fuel source.
- Fifty wt% MnCl<sub>2</sub> on super-activated carbon IRH-33 is an effective and regenerable sorbent to scrub ammonia from H<sub>2</sub> produced during the thermolysis of AB.
- A procedure needs to be developed for sizing the particulate filter area in cryo-adsorption systems in order to contain sorbent and meet SAE purity standards.
- The efficiency of the GLS was shown to be strongly dependent on flow rate, pressure and temperature. Operating conditions were determined that minimized liquid carry-over to <100 ppm of the inlet oil mass.

Future work in Phase 3 will comprise:

- Lead integrated power plant/storage system modeling technical area.
- Collaborate with SRNL and NREL on making the Simulink framework available on the HSECoE website.
- Update high level models to reflect the as-fabricated behavior of the cryo-adsorption system and assess its impact on the power plant performance.
- Incorporate updated chemical hydrogen storage system model in Simulink framework after LANL/PNNL have collected and analyzed their latest kinetic data.

- Collaborate with Ford/BASF on qualitative risk assessments of cryo-adsorption system.
- Engineering and testing of specialty components for H<sub>2</sub> storage systems and their experimental evaluation, such as the particulate filter in the cryo-adsorption system.
- Orderly completion of the GLS and ammonia filter development for the chemical hydrogen storage system, with an emphasis on collecting data for model validation.
- Publish results in peer reviewed journals.

## FY 2013 PUBLICATIONS/PRESENTATIONS

1. José Miguel Pasini and Bart A. van Hassel, Vehicle Simulation Framework: Graphical User Interface, Face-To-Face 9 Meeting HSECoE, Mystic, CT, October 9–11, 2012.
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3. Jagadeswara Reddy Karra and Bart A. van Hassel, H<sub>2</sub> Quality, Face-To-Face 9 Meeting HSECoE, Mystic, CT, October 9–11, 2012.
4. John Khalil, MOF-5 Safety Testing, Face-To-Face 9 Meeting HSECoE, Mystic, CT, October 9–11, 2012.
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6. B.A. van Hassel, R. McGee, R. Karra, J. Khalil, R. Brown, A. Murray, Engineering Aspects of Materials Based Hydrogen Storage Systems, IEA Task 32 Kyoto, Japan, October 26–27, 2012.
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11. Igor I. Fedchenia, Bart A. van Hassel and Ron Brown, Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H<sub>2</sub> Storage Materials, submitted to Inverse Problems in Science and Engineering.
12. José Miguel Pasini, Claudio Corgnale, Bart A. van Hassel, Theodore Motyka, Sudarshan Kumar, and Kevin L. Simmons, "Metal hydride material requirements for automotive hydrogen storage systems," Accepted by Int. J. Hydrogen Energy, vol. 38, pp. 9755-9765 (2013).
13. Bart A. van Hassel, Jagadeswara. R. Karra, David Gerlach, and Igor I. Fedchenia, Dynamics of fixed-bed adsorption of ammonia on impregnated activated carbon for hydrogen purification, to be submitted to Separation and Purification Technology.

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2. 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.
3. Bart van Hassel, Jose Miguel Pasini, Andi Limarga, John Holowczak, Igor Fedchenia, John Khalil, Reddy Karra, Ron Brown, Randy McGee, Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage, Annual Report of UTRC's contribution to HSECoE project, July, 2012.
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