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

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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 Storage 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) 2014 Objectives

- Develop vehicle/power plant/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 materials-based hydrogen storage systems
- Assess the viability of onboard purification for various storage material classes and purification approaches
- Collaborate closely with the HSECoE partners to advance materials-based hydrogen storage system technologies

Technical Barriers

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

(A) System Weight and Volume

(D) Durability/Operability

(H) Balance-of-Plant (BOP) Components

Technical Targets

The goals of this project mirror those of the HSECoE to advance hydrogen storage system technologies toward the DOE Hydrogen Storage Program's 2017 storage targets [1]. UTRC reduced the mass and volume of its contribution to the BOP components from 28% to <5% by mass and from 12% to <3% by volume of the total chemical hydrogen storage system. Thereby the gravimetric capacity of the chemical hydrogen storage system was improved from 31 g H_2/kg system to 41 g H_2/kg system which is somewhat below the 2017 gravimetric capacity target of 55 g H_2/kg system. Thereby the volumetric capacity of the chemical hydrogen storage system was improved from 36 gram H_2/L system to 40 gram H_2/L system, which is the 2017 target. The status of UTRC's technical targets is documented in Table 1.

FY 2014 Accomplishments

Accomplishments during the current project period include:

- Collaborated with HSECoE partners on disseminating the Simulink® Framework with a graphical user interface (GUI) on the Web.
- Implemented Pacific Northwest National Laboratory's (PNNL's) chemical hydrogen storage (CH) system model in the Simulink® Framework and made it available for beta testing.
- Tested, at high pressure (12-16 bar), the performance of a compact gas/liquid separator (GLS) that was designed for the CH system. The GLS is capable of separating hydrogen gas from the fluid up to a peak power level of 80 kWe, as required for a light-duty vehicle.

TABLE 1. UTRC's Progress towards Meeting Technical Targets for Onboard H_2 Storage Systems

	Characteristic	Units	2017 Target	UTRC
Chemical H_2 storage system	Gravimetric capacity	kWh/kg (kg H_2/ kg system)	1.8 (0.055)	1.3 (0.041)
	Volumetric capacity	kWh/L (kg H_2/L system)	1.3 (0.04)	1.3 (0.04)
Cryo-adsorbent H_2 storage system	H_2 Quality	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)	Meets

SAE – SAE International (automotive standards association)
ISO – International Organization for Standardization

- Validated a computational fluid dynamics (CFD) model of the GLS by measuring the critical gas velocity and the droplet size distribution at the outlet of the GLS.
- Identified and quantified impurities that result from using silicone oil AR20 as the liquid for making a slurry with ammonia borane (NH_3BH_3) or alane (AlH_3). Identified fluids with a significant lower vapor pressure and higher thermal stability, which may be more suitable than AR20.
- Characterized metal-organic framework-5 (MOF-5) particulate filters for the cryo-adsorbent hydrogen storage system in terms of particulate filtration efficiency, darcy flow coefficient and thermal shock resistance.

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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, low-pressure 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 hydrogen storage for automotive applications. During the fifth year of the HSECoE project, UTRC continued the successful development of the Simulink® modeling framework for comparing H_2 storage systems on a common basis, which can now be downloaded from the National Renewable Energy Laboratory (NREL)-hosted website at www.hsecoe.org. UTRC completed its contribution to the chemical hydrogen storage system development in an orderly fashion when DOE decided to discontinue the development of such a system after the Phase 2 to Phase 3 Go/No-Go meeting in March, 2013. Through experimental work, UTRC determined the critical velocity of a compact GLS at elevated pressure with a surrogate gas (N_2). The result show that this particular GLS design was capable of separating H_2 gas from the fluid at a power level of up to 80 kWe, which is the full-scale capacity for a light-duty automotive system. UTRC also developed a CFD model of the GLS in order to predict the liquid carryover as a function of operating conditions. The model was validated with the experimental results of liquid carryover rate as a function of gas flow rate and through the measurement of the droplet size distribution at the outlet of the vortex finder. UTRC demonstrated through simulated distillation and vapor pressure measurements with an isoteniscope that the silicone oil AR20 had an unacceptable high vapor pressure for this application and recommended alternate fluids with a significant lower vapor pressure and higher boiling point but similar viscosity. For the cryo-adsorption system, UTRC evaluated several particulate filters for the mitigation of MOF-5 particulates and demonstrated that those filters did remove particulates between 0.2 um and 32 um to concentrations that were orders of magnitude lower than the SAE guideline [2]. The filters were also tested for their flow resistance and their ability to withstand thermal cycling between room temperature and 77 K. It is expected that the allowable pressure drop in the system will ultimately determine how much particulate filter area needs to be installed.

RESULTS

The Simulink® Framework with a GUI was disseminated on the Web through NREL's website at www.hsecoe.org. It contains models of the 350-bar and 700-bar compressed gas storage systems and the model of the ideal metal hydride. Users can vary the metal hydride amount and the buffer

volume when simulating different drive cycles. UTRC also incorporated PNNL's chemical hydrogen storage system into the framework. It will first be beta-tested before it will become available on the website. A diagram of the GUI is shown in Figure 1.

A chemical hydrogen storage system that uses a liquid hydrogen carrier requires a GLS in order to separate the hydrogen gas from the spent liquid hydrogen carrier. UTRC relentlessly reduced the weight and volume of the GLS in order to substantially improve the gravimetric and volumetric capacity of the chemical hydrogen storage system from 31 g H_2/kg system to 41 g H_2/kg system and from 36 gram H_2/L system to 40 gram H_2/L system, which is the 2017 volumetric capacity target. The compact GLS with a low profile was tested at high pressure (12 and 16 bar) and at a capacity that is required for a full size automotive chemical hydrogen storage system that can support a peak fuel cell power of 80 kWe. Figure 2 shows the excellent performance of the GLS at two different pressures (12 and 16 bar) and two different silicone oil AR20 flow rates as a function of the flow rate of the surrogate gas (N_2 instead of H_2). The GLS meets the S*M*A*R*T milestone requirements with its critical N_2 gas flow rate of about 300 slpm under those experimental conditions. The critical gas velocity for H_2 gas

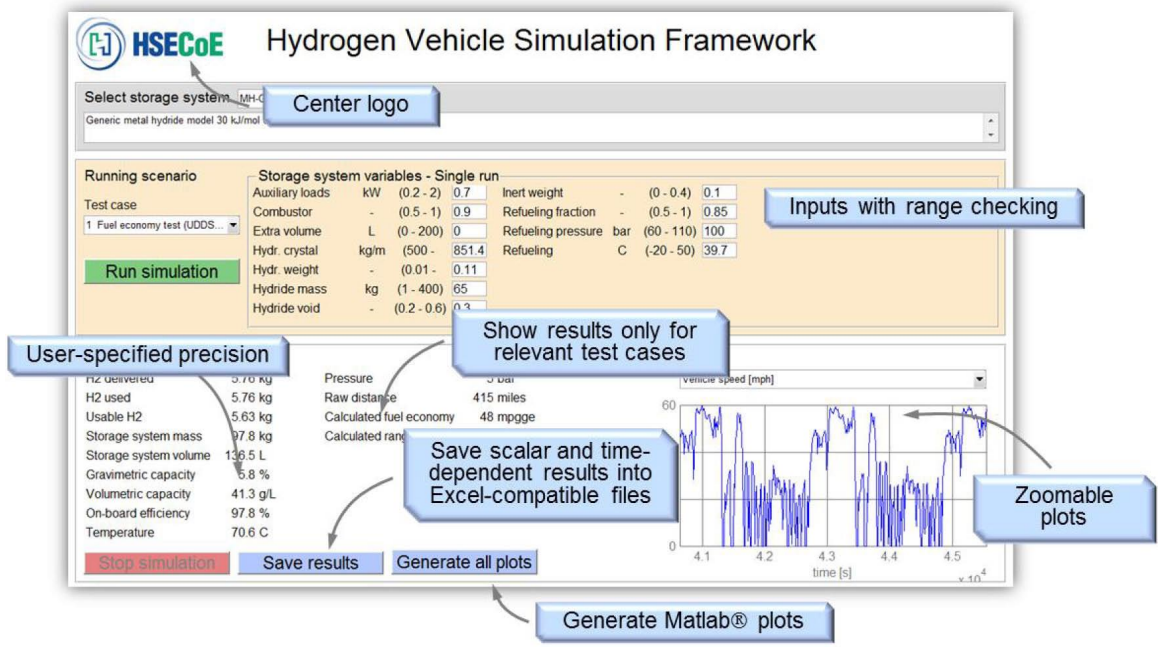

FIGURE 1. Example of GUI of Simulink® modeling framework.

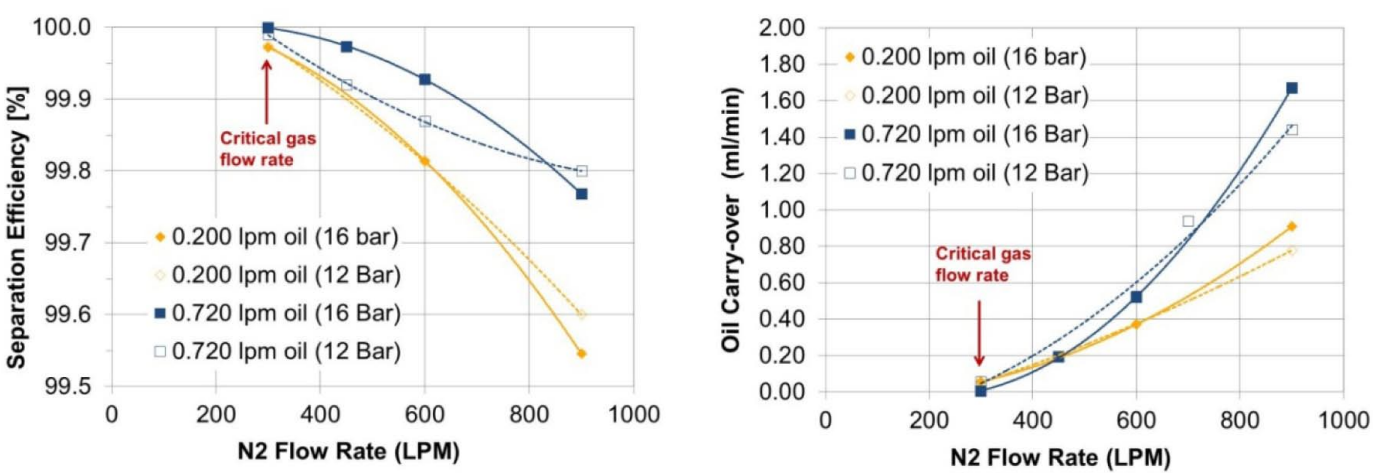

FIGURE 2. Silicone oil AR20 carryover rate (ml/min) as a function of the N_2 gas flow rate (slpm) at 70°C and elevated pressure (12-16 bar) for two different silicone oil flow rates.

is expected to be a factor 3.75 higher than for N_2 gas. This means that this GLS will be able to separate H_2 from silicone oil up to an electrical power level of about 80 kWe by the proton exchange membrane fuel cell. In other words, the GLS that was developed and tested has a capacity that is sufficient for this light-duty vehicle application.

The GLS is such an important unit operation in the chemical hydrogen storage system that a CFD model was developed of this component in order to develop the capability to size it for different capacities, e.g. for the capacity that would have been required for the Phase 3 sub-scale prototype. Figure 3 shows the streamlines of droplets in the GLS. Droplets that hit the wall will form an oil film that will drain. Dry gas is extracted from the center of the vortex with a vortex finder. The model correctly predicted the critical gas flow rate below which the liquid carryover rate is negligible. The CFD model predicted an outlet droplet size distribution in the size range of 10-50 micrometer but droplet size distribution measurements showed a droplet size distribution in the range of 100-500 micrometer, as shown in Figure 4. A more detailed computational analysis showed that the 10-50 micrometer droplets would form an oil film on the inside surface of the vortex finder and the oil film would breakup into 100-200 micrometer droplets due to the high gas flow rate in the vortex finder.

Delivering hydrogen from a materials-based hydrogen storage system at a high quality is of key importance for the long-term stability of the expensive proton exchange membrane fuel cell. UTRC noticed during tests with the GLS that the silicone oil AR20 posed significant challenges as the optical window for droplet size distribution measurements quickly became contaminated with an oil film. This prompted an investigation of the boiling point range and vapor pressure of silicone oil AR20, as shown in Figure 5. Simulated distillation showed a relative low boiling point range in comparison to the expected operating conditions in the thermolysis reactor (120-200°C) and measurements with the isoteniscope showed a high vapor pressure, which is clearly undesired. Dow Chemical assisted with additional qualitative and quantitative measurements of the different siloxane species that are present in the gas phase, as documented in Table 2. These impurities would need to be adsorbed similar to the other impurities like borazine, diborane and ammonia when using a fluid form of AB. A better approach is to select fluids with a much lower vapor pressure and higher boiling temperature range. Several of such oils have been identified and were included in Figure 5 but it will need to be determined how well (chemical) hydrogen storage material will disperse in such fluids.

In the good spirit of the HSECoE, UTRC also contributed to the development of the cryo-adsorbent system by evaluating the performance of porous metal particulate filters when exposed to MOF-5 adsorbent. The sorbent was located in the bottom of a transparent pressure vessel at the start of the experiment and fluidized by nitrogen gas, as a surrogate for hydrogen gas. Gradually MOF-5 particulates would start accumulating on the filter surface and form a filter cake. Filter cake formation caused a drop in the Darcy

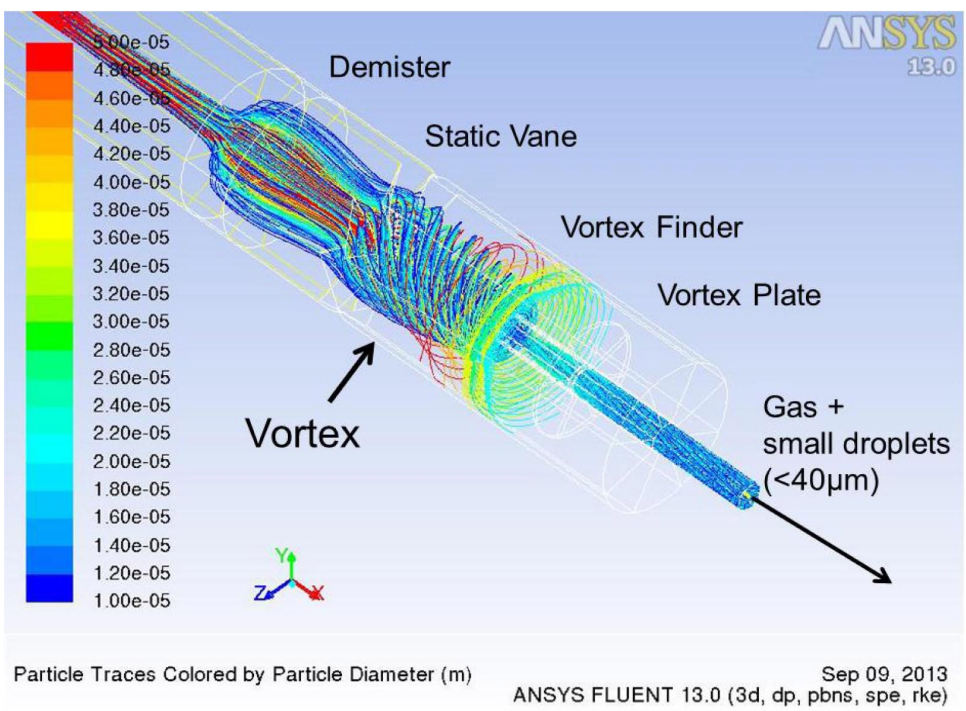

FIGURE 3. CFD model of the GLS. The streamlines of the droplets have been colored by their droplet size.

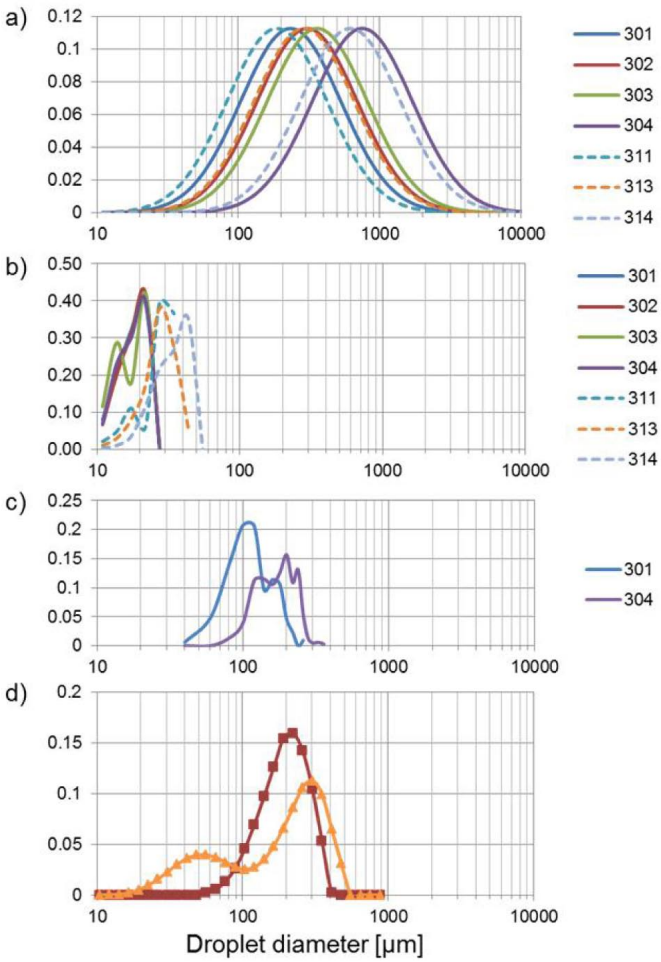

FIGURE 4. Droplet size distributions at 70°C, 12 bar and various N_2 and silicone AR-20 flow rates (Table 2): a) Inlet of the GLS, b) Outlet of the GLS (no filming), c) Outlet of the GLS with filming inside the vortex finder, d) Two representative but distinctly different experimental droplet size distributions at a N_2 gas flow rate of 600 slpm and a silicone oil AR20 flow rate of 0.365 lpm.

TABLE 2. Quantitative Results of Headspace Gas Chromatography with Flame Ionization Detection Of Silicone Oil AR20 at 70°C, as used in the AB Slurry of the Chemical Hydrogen Storage System

Component	MW (g/mol)	ppm by weight	ppm by volume (25°C, 1 atm)
Me_3SiOH	90	318	106
$Me_3SiOSiMe_2OH$	164	86	16
$Me_3Si(OSiMe_2)OSiMe_2OH$	238	20	2
$Me_3Si(OSiMe_2)_2OSiMe_2OH$	312	7	0.7
$Me_3Si(OSiMe_2)_3OSiMe_2OH$	386	12	0.9
cyclo$(OSiMe_2)_4$(OSiMePh)??	432	33	2
cyclo$(OSiMe_2)_5$(OSiMePh)??	506	23	1

flow permeability of the filter (Figure 6), which needs to be considered in the overall system analysis of a cryo-adsorbent system. The porous metal filters were able to reduce the particulate content well below the SAE guideline of 1,000 µg/m^3, as shown in Figure 7. The porous metal filters did also withstand rapid thermal cycles between room temperature and 77 K as evidenced by no change in physical appearance or Darcy flow permeability. The Darcy flow permeability can be used to right-size the particulate filter area for flow through cooling when the team determines a value for the allowable pressure drop.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2014 are:

- Users of the Simulink® modeling framework will benefit from having access to more hydrogen storage system model parameters in the GUI.

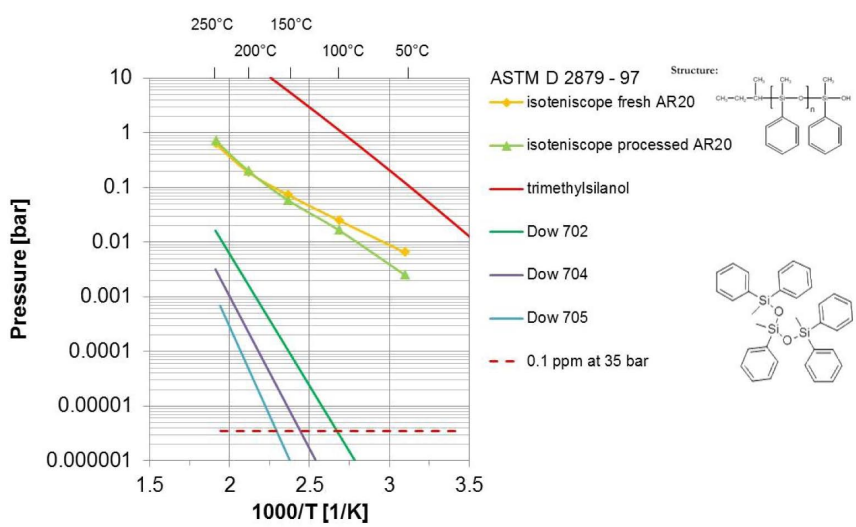

FIGURE 5. Boiling temperature range (simulated distillation) and vapor pressure (isoteniscope) of silicone oil AR20 as a function of temperature.

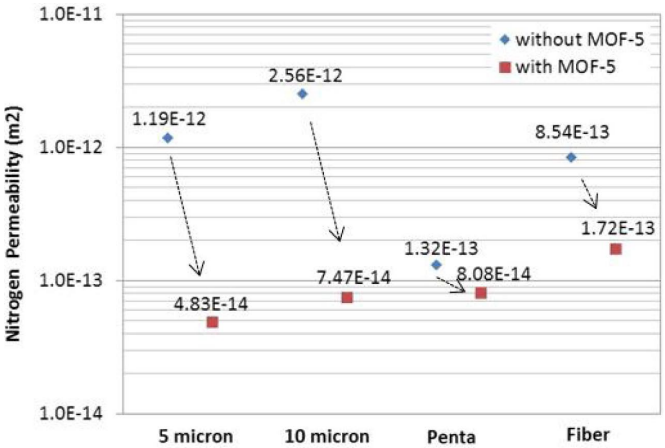

FIGURE 6. Drop in Darcy flow parameter due to filter cake formation for four different porous metal filters.

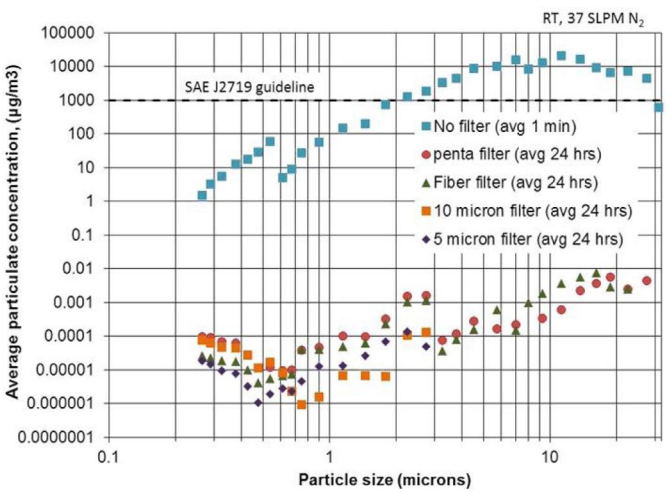

FIGURE 7. Particulate concentration at the outlet of the particulate filters when exposed to MOF-5 particulates.

- Silicone oil AR20 is unsuitable for turning AB into a slurry as its boiling point is too low. This causes a very high vapor pressure and contamination of the hydrogen gas that is liberated in the thermolysis reactor.
- Gas liquid separators that use a combination of gravitational settling, coalescence and a centrifugal force enable an efficient separation of gas and liquid for systems with fluid-phase chemical hydrogen storage materials.
- Surface filters on which MOF-5 particulates will form a filter cake are suitable for reducing the particulate concentration to levels that are well below the SAE guideline and it is the allowable pressure drop that will ultimately determine how much filter area needs to be installed.

Future work in Phase 3 will comprise:

- Lead Integrated Power Plant/Storage System Modeling technical area.
- Collaborate with Savannah River National Laboratory and NREL on making the newest version of the Simulink® Framework available on the HSECoE website.
- Incorporate updated CH system model in Simulink® Framework after Los Alamos National Laboratory/ PNNL have collected and analyzed their latest kinetic data.
- Update high level models to reflect the as-fabricated behavior of the cryo-adsorption system and assess its impact on the power plant performance.
- Document results in final reports about UTRC's contribution to the metal hydride, chemical hydride and the cryo-adsorption system developments.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Bart A. van Hassel, Jagadeswara R. Karra, Jose Santana, Salvatore Saita, Allen Murray and Daniel Goberman, Richard Chahine and Daniel Cossement, Ammonia Sorbent Development for On-Board H_2 Purification, Accepted by Separation and Purification Technology.

2. Igor I. Fedchenia, Bart A. van Hassel and Ron Brown, Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H_2 Storage Materials, Accepted by Inverse Problems in Science & Engineering.

3. 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, In Preparation.

4. B.A. van Hassel, R. McGee, R. Karra, A. Murray, I. Fedchenia, D. Gerlach, and Jose Miguel Pasini, Engineering Aspects of Materials Based Hydrogen Storage Systems, IEA Task 32, Heraklion, Greece, April 22–25, 2013.

5. B.A. van Hassel, Hydrogen Storage Systems for Mobile Applications, IEA Task 32, Key Largo, Florida, USA, December 8–12, 2013.

6. B.A. van Hassel, Hydrogen Storage for Mobile Applications in US, I2CNER International Workshop, Hydrogen Storage, Kyushu University, Fukuoka, Japan, January 31, 2014, Invited Talk.

7. Bart A. van Hassel, Randy McGee, Allen Murray and Shiling Zhang, Engineering Technologies for Fluid Chemical Hydrogen Storage System, MCARE 2014, Clearwater, Florida, February 17–20, 2014, Invited Talk.

8. K.P. Brooks, T.A. Semelsberger, K.L. Simmons and B.A. van Hassel, Slurry-based chemical hydrogen storage systems for automotive fuel cell applications, Submitted to Energy & Fuels Journal.

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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.