

Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

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United Technologies Research Center



DOE Hydrogen Program

Annual Merit Review

Washington, DC

May 14, 2013

Project ID: ST006



Overview

■ Timeline

- Start: February 2009
- End Phase 1: March 2011
- End Phase 2: June 2013
- End Phase 3 / Project: June 2014
- Percent complete: 83% (spending)

■ Budget

- \$5.91M Total Program
 - Reflects budget reduction with \$0.95M
 - \$4.58M DOE
 - \$1.33M (22.5%) UTRC
- FY09: \$600k DOE
- FY10: \$1,000k DOE
- FY11: \$750k DOE
- FY12: \$750k DOE
- FY13: \$775k DOE

■ Barriers*

- A – J
- A. System Weight & Volume
- D. Durability/Operability
- J. Thermal Management

■ Targets*

- All

■ Partners



Objectives

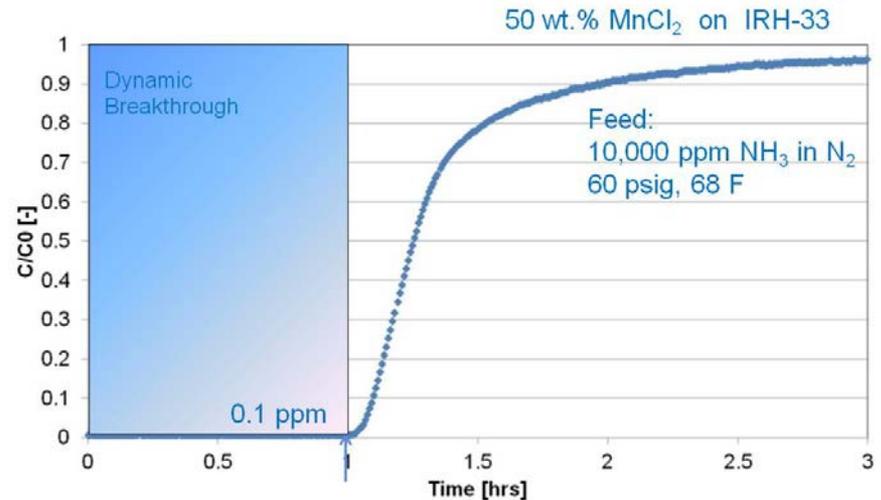
- Design of materials-based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles.

Performance Measure	Units	2010	2017	Ultimate
System Gravimetric Capacity	g H ₂ /kg system	45	55	75
System Volumetric Capacity	g H ₂ /L system	28	40	70
System fill time (for 5 kg H ₂)	minutes	4.2	3.3	2.5
Fuel Purity	% H ₂	SAE J2719 guideline (99.97% dry basis)		

- Major project impact:
 - Gas/Liquid separation (GLS) of liquid chemical hydride
 - H₂ quality (NH₃ adsorbent, particulate filter)
 - Integrated Power Plant Storage System Modeling:
 - UTRC oversees modeling framework on consistent platform, supports storage system model integration and develops GUI
 - Risk Assessment: MOF-5 test plan and AB flammability

Phase 2 S*M*A*R*T Milestones and Status

Partner	S*M*A*R*T Milestone	Status
UTRC	Demonstrate less than 100 ppm liquid carry-over with gas/liquid separator with weight less than 5.4 kg and volume less than 19 liters.	Carry-over: 800±200 ppm (70°C, 12 bar) Mass 5.8 kg Volume 2.7 Liter
UTRC	NH ₃ filter capable of 1800 miles fuel cell grade H ₂ with a maximum mass of 1.2 kg and a maximum volume of 1.6 liters.	Demonstrated: 0.1 ppm NH ₃ Mass 1.1 kg Volume 1.6 L



Approach

- Gas liquid separator (GLS):
 - Selected and scaled down a GLS through collaboration with vendor
 - Demonstrated the engineering concept through testing with surrogate materials
 - Developed GLS model and UTRC is performing model validation tests
- H₂ quality:
 - Collected experience data from partners about particulate mitigation in flow through cryo-adsorbent systems
 - Developed NH₃ filter and provided filters for testing at LANL in combination with other impurities (competitive adsorption with borazine)
 - Developed NH₃ sorbent filter model and validated model
- Simulink[®] Framework:
 - Developed graphical user interface (GUI) architecture and performed beta-test
 - Compared H₂ storage systems on a common basis, including all BOP (PNNL)
- Risk assessment:
 - Performed flammability tests of AB slurries at UTRC
 - Developed detailed test plan for MOF-5 risk assessment at Ford/BASF

Use results to estimate material property requirement for DOE's 2017 system level targets.

Collaborations



- MOF-5 risk assessment
- Particulate mitigation



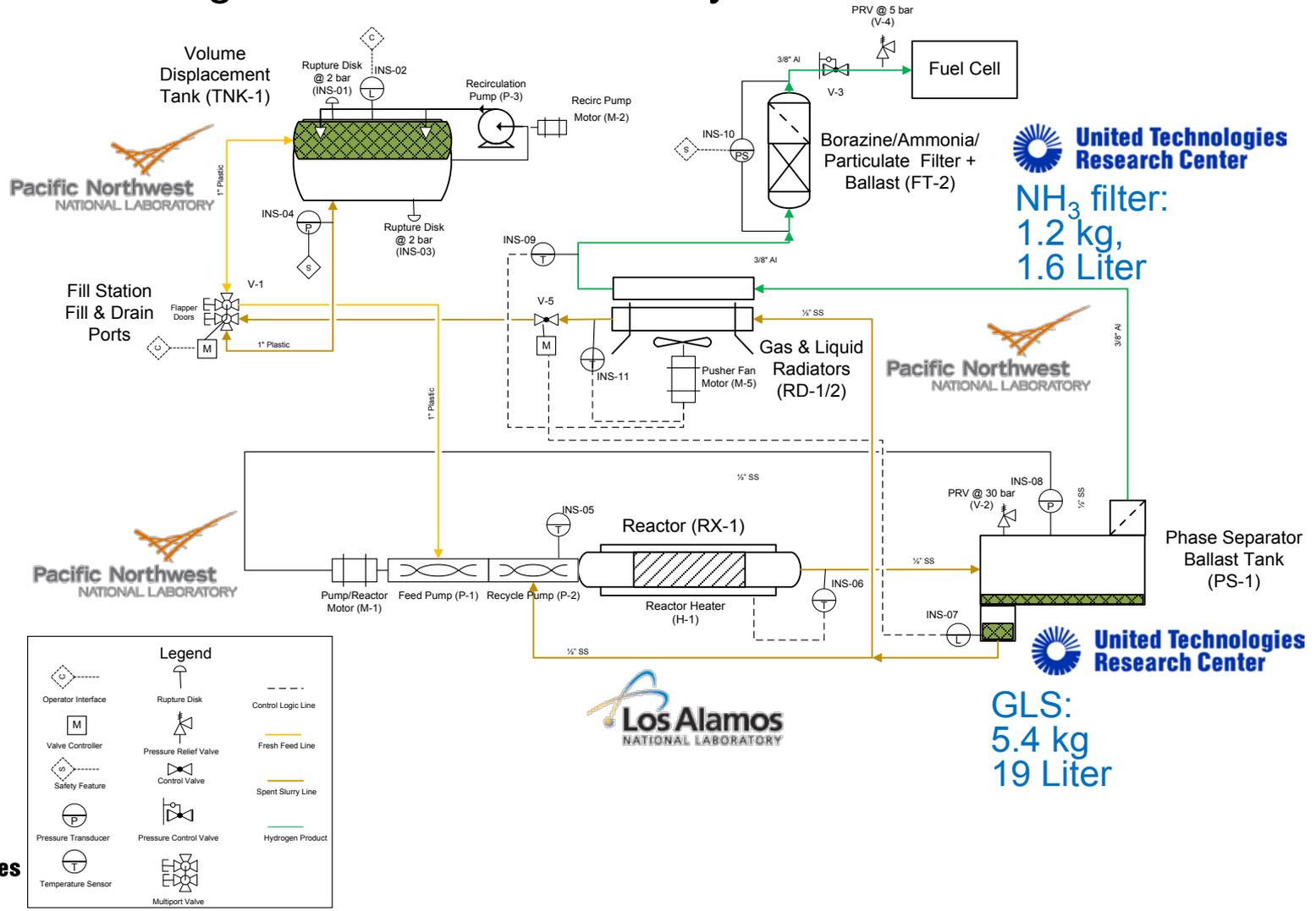
- Process development
- BOP components
- Testing of GLS with surrogate material
- IRH-33 as support in NH_3 sorption filter
- NH_3 filter performance tests
- Risk assessment: AB flammability



- Comparison of H_2 storage systems on a common basis
- Integration of storage system models in framework
- Graphical user interface development for Simulink[®] framework and beta-test with ORNL and SNL

Demonstrate Engineering Concepts

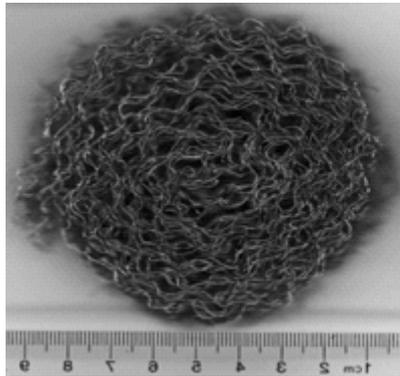
- Hydrogen gas must be separated from the liquid spent fuel and purified on-board following the exothermic thermolysis of ammonia borane



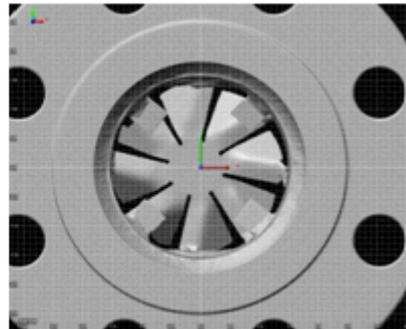
Gas Liquid Separation for Chemical Hydrides

- GLS design features:

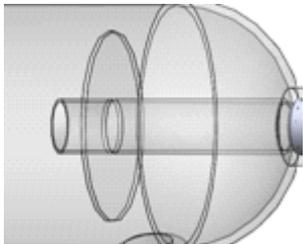
Demister pad



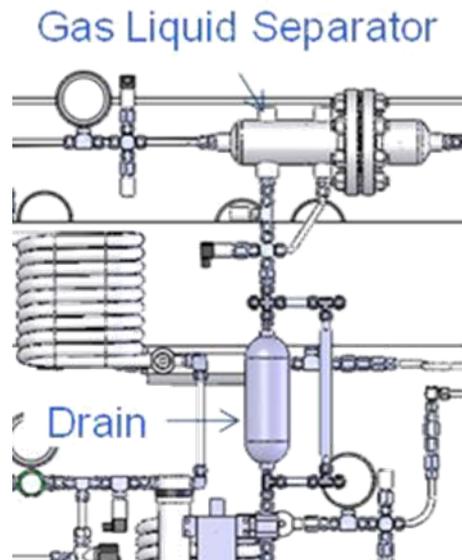
Static vane pack induces a swirl



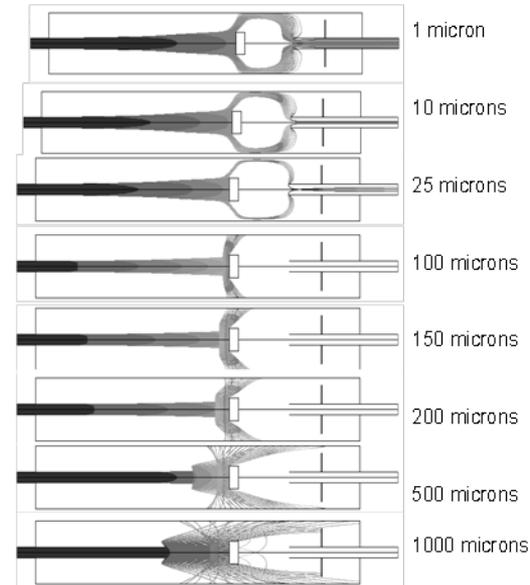
Vortex finder



Surrogate spent fuel reservoir with drain and level control



- Droplet transport model developed in order to improve GLS design

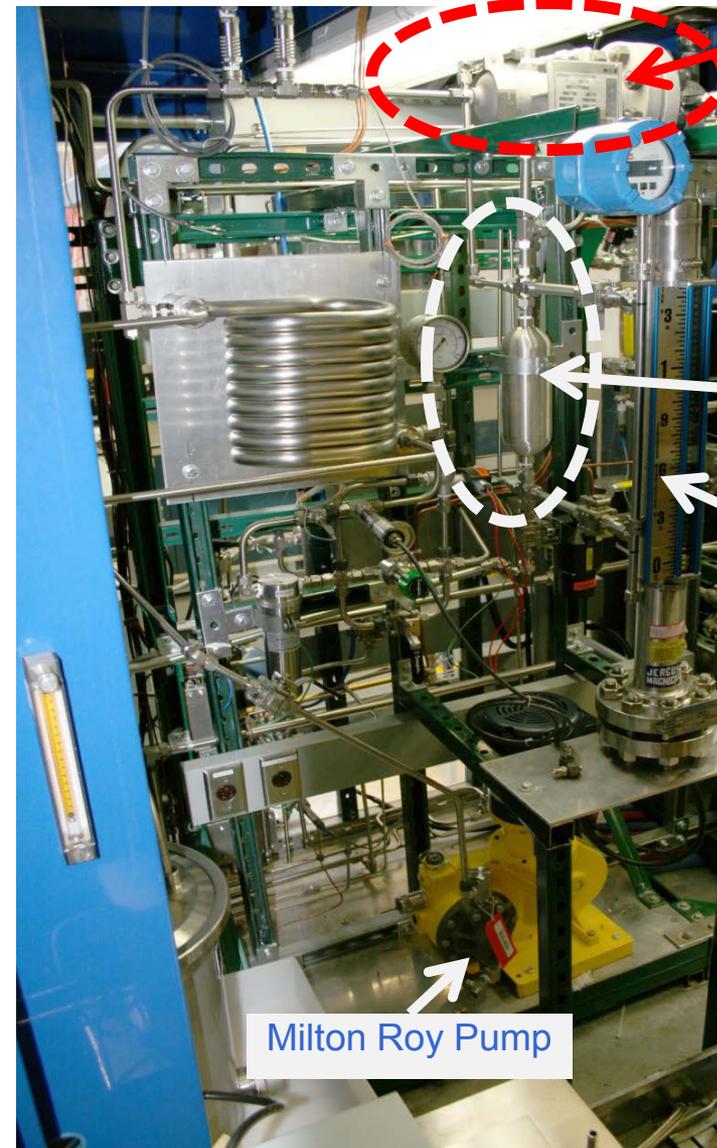


Validate model with droplet size distribution measurement in outlet



Gas Liquid Separator (GLS) Test Facility at UTRC

- Constructed gas-liquid separator test facility
- Completed test facility shake down:
 - N₂ as surrogate for H₂
 - Silicone oil and polyimide (slurry) as surrogate for liquid chemical hydride (silicone oil tested as of March 2013)
 - Mahr pump (Low weight and volume) limits pressure to 200 psig (13.8 bar)
- Demonstrated S*M*A*R*T milestone target with silicone oil



Gas Liquid Separator

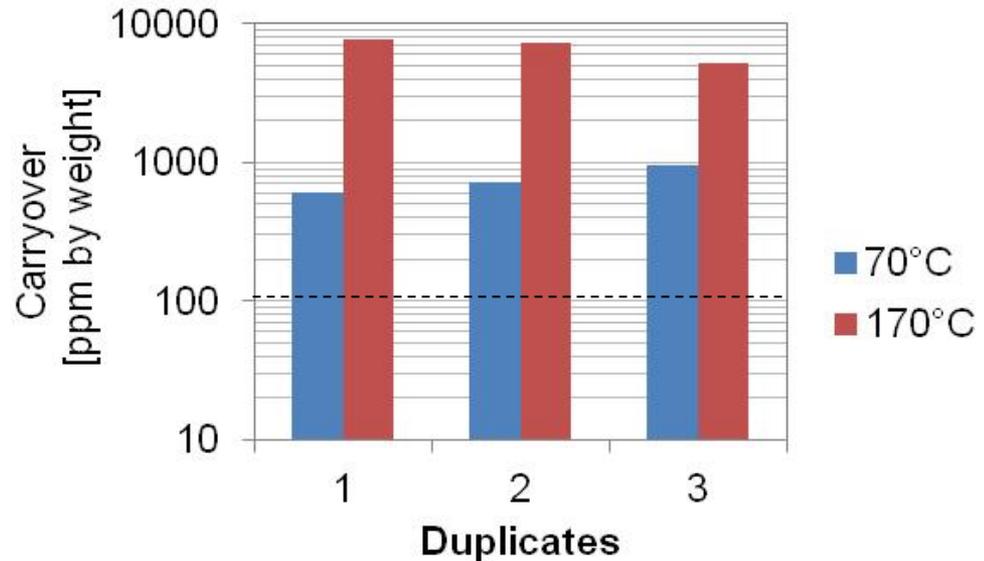
Drain

Level Indicator

Milton Roy Pump

GLS Results

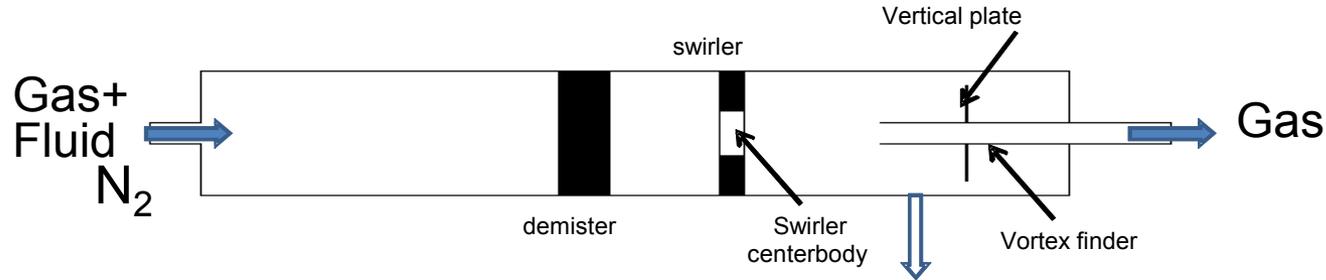
- Tested performance of custom-designed gas-liquid separator under the agreed upon S*M*A*R*T milestone conditions:
 - 720 mL/min liquid phase and 600 L/min of H₂ @ STP (40 wt% AB @ 2.35 Eq H₂ and max H₂ flow of 0.8 g/s H₂) ... less than 100 ppm aerosol.....
- Partial design of experiment with factors:
 - Gas flow rate
 - Oil flow rate
 - Temperature (highlighted)
 - Pressure
 - Particulate matter weight fraction in slurry
- Carryover:
 - Droplets vs. vapor condensation:
 - Low vapor pressure is an important fluid chemical hydride material property



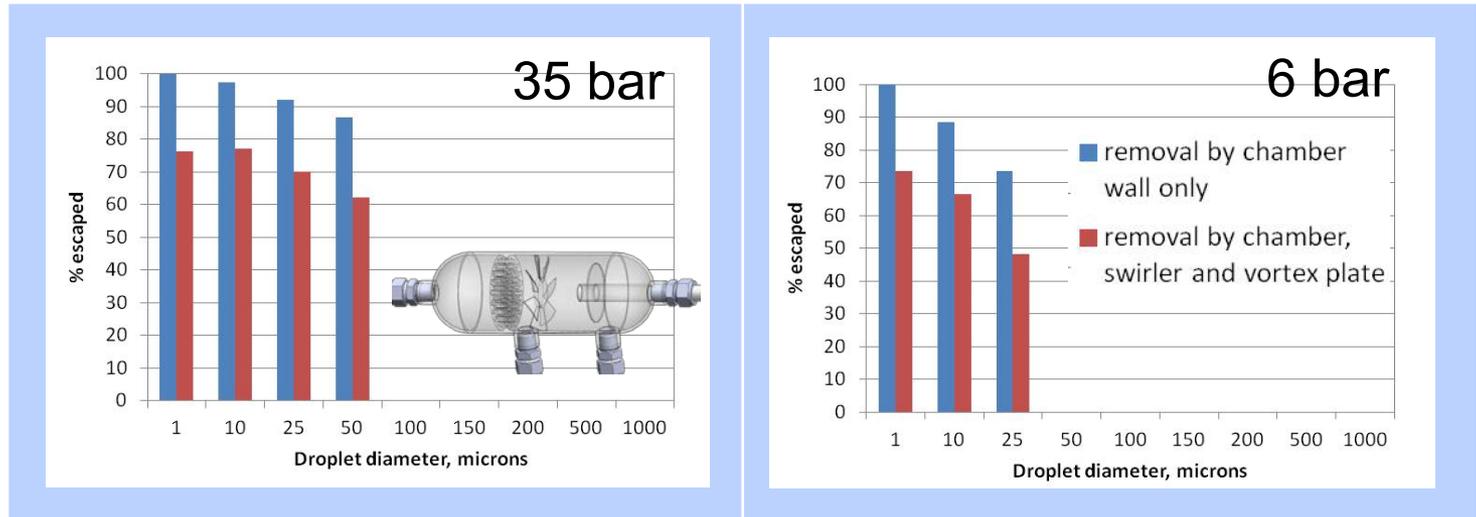
Temperature [°C]	Carryover in mass ppm			Average ppm
	1	2	3	
70	603	724	956	$(8 \pm 2) \cdot 10^2$
170	7808	7189	5192	$(7 \pm 1) \cdot 10^3$

GLS Model Development

- Developed axisymmetric Fluent model with droplet tracking in support of gas-liquid separator optimization:



S*M*A*R*T:
 Gas:
 600 slpm,
 Liquid:
 0.72 slpm
 at 170°C

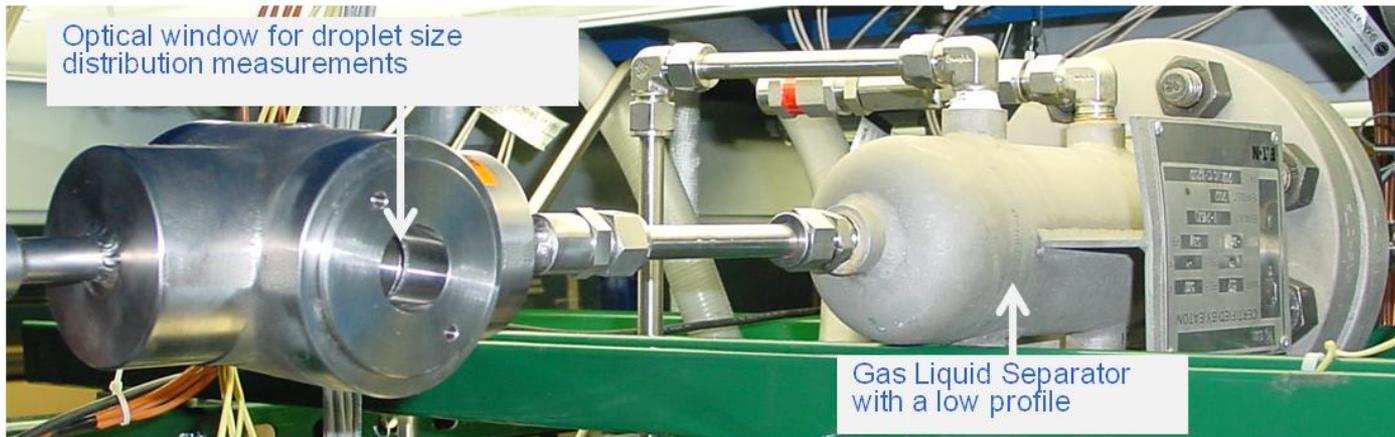


- Determined need for coalescence filter to remove small droplets

Knowledge gap: Droplet size distribution at GLS inlet

Technical Accomplishments (Cont.)

- Obtained operating experience with GLS system
- Developed capability to determine droplet size distribution at outlet of gas-liquid separator for model validation:

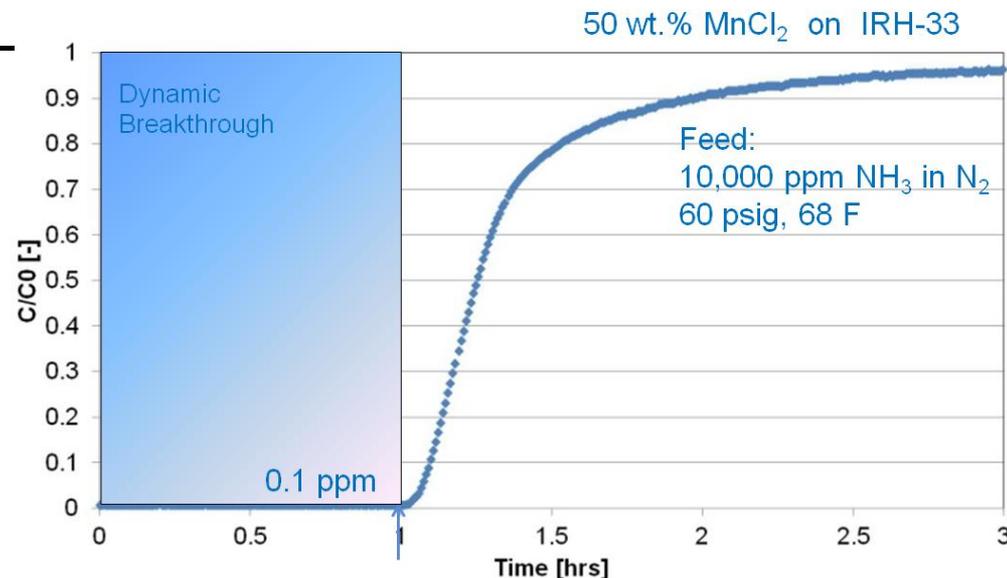


- Developed capability to design gas-liquid separator for Phase 3
- Identified drain and level control system as opportunities for integration with gas-liquid separator in order to reduce weight and volume
- Recommended further integration between thermolysis reactor and gas-liquid separator

Ammonia Filter

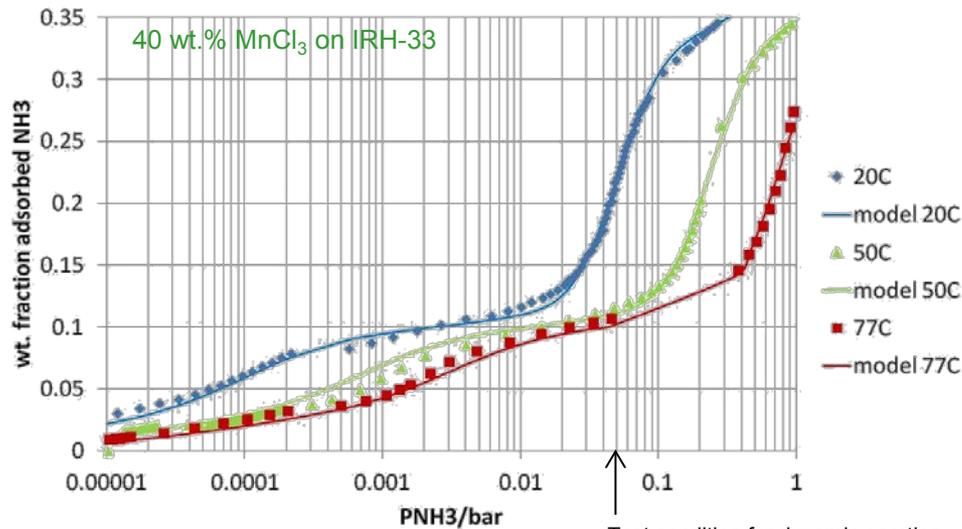
(On-board impurity mitigation)

- Optimize MnCl_2 loading on super-activated carbon IRH-33 (UQTR) for dynamic adsorption of NH_3
 - Develop and validate dynamic breakthrough adsorption model
 - Size filter for 1800 miles
 - Provide NH_3 filters of competitive adsorption test with ammonia + borazine mixtures to LANL
-
- Apply learning from evaluating particulate filters for cryo-adsorption system ($<10\mu\text{m}$, $<1\mu\text{g/L}$)

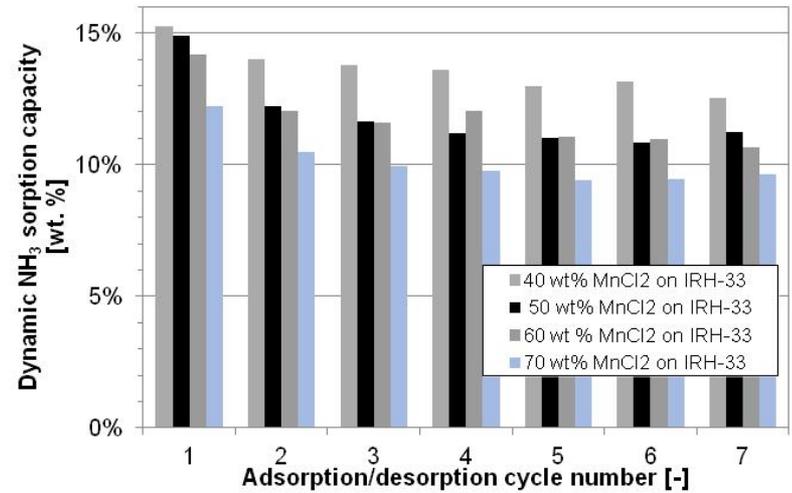


NH₃ Sorbent Filter Results

- Demonstrated S*M*A*R*T milestone of NH₃ filter:
 - ...Ammonia scrubber with a minimum replacement interval of 1800 miles... outlet concentration of 0.1 ppm (inlet concentration = 500 ppm)< 1.2 kg and < 1.6 liter.....
- Characterized NH₃ adsorption isotherm (-20, 0, 20, 50, 77°C)
- Optimized capacity and demonstrated sorbent regeneration

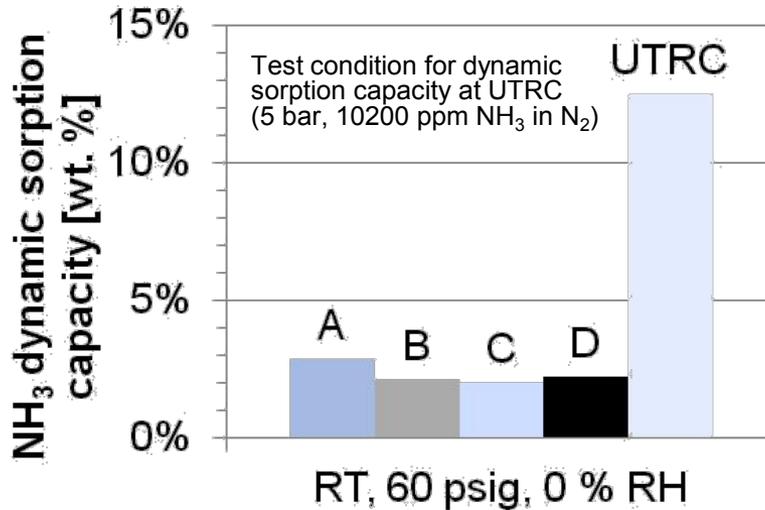


↑ Test condition for dynamic sorption capacity at UTRC (5 bar, 10200 ppm NH₃ in N₂)



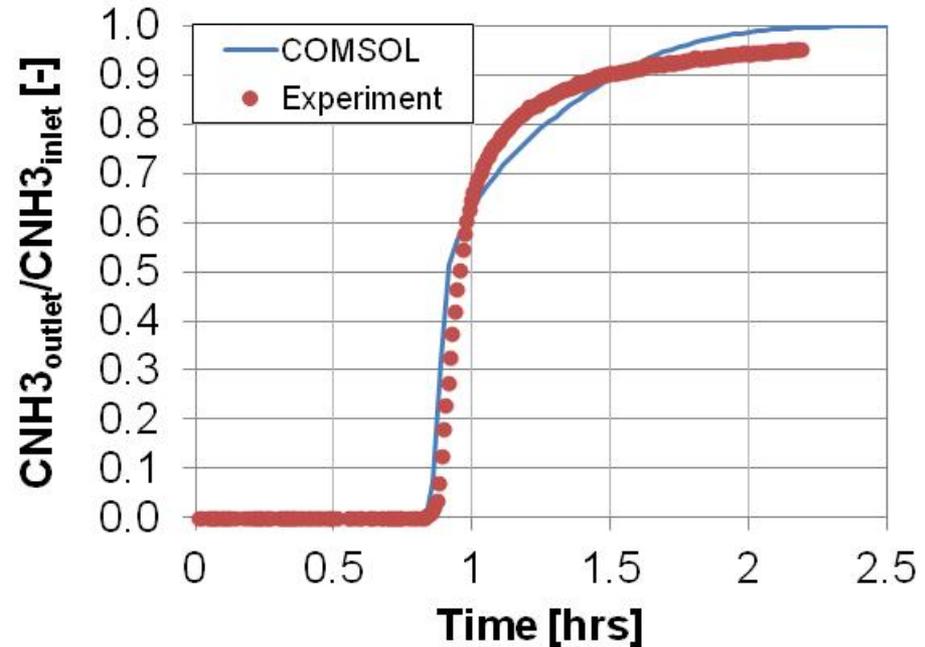
Dynamic NH₃ Sorption Capacity

- Demonstrated substantial ammonia capacity improvement (6x) over commercially available sorbents



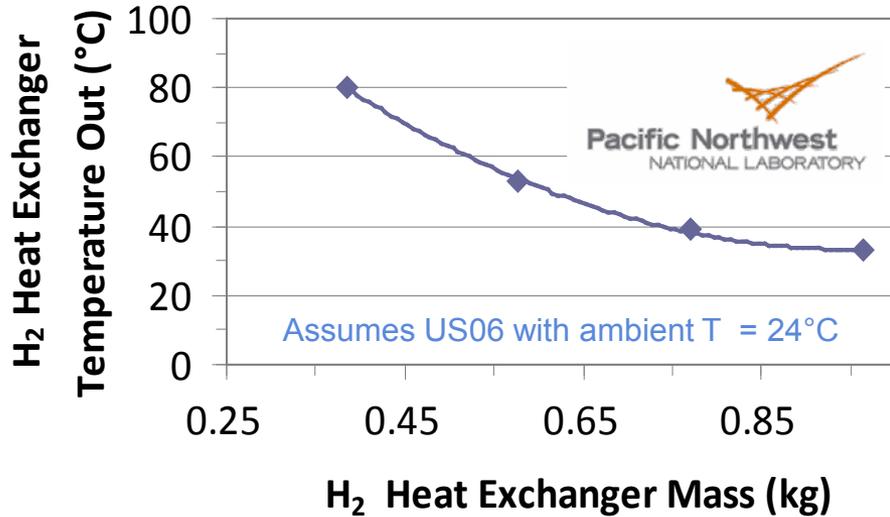
Ammonia Filter with 50 wt% MnCl₂ on IRH-33 meets weight and volume targets of HSECoE

- Developed and validated dynamic adsorption breakthrough model

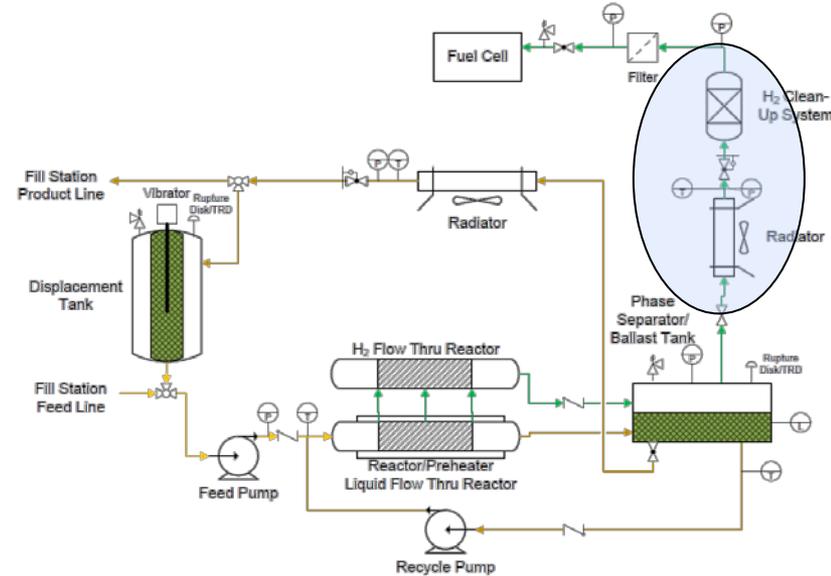


Demonstrated that ammonia can be adsorbed to produce fuel-cell grade hydrogen

Minimizing NH₃ filter and H₂ gas cooler weight



Chemical Hydride Storage and Reaction System
February 1, 2012



Radiator outlet temperature or Inlet temperature of adsorbent bed (°C)	Heat exchanger weight (kg)	Dynamic NH ₃ sorption capacity (wt%)	NH ₃ filter weight (kg)	Total weight (filter + Heat exchanger) (kg)
23	0.965	11.25	1.1	2.07
50	0.577	9.31	1.3	1.88
80	0.385	8.71	1.5	1.86

Slight advantage of warm gas (80 °C) cleanup*.
(* Borazine filter components not yet included)

Framework with Graphical User Interface (GUI)

- Metal hydride storage system model example in Simulink® framework

Hydrogen Vehicle Simulation Framework

Select storage system: MH-GH3s v3

Generic metal hydride model 30 kJ/mol enthalpy of dehydrogenation.

Running scenario

Type of run

Single run

Multiple (parameter sweep)

Compare different systems

Test case: 1 Fuel economy test ...

Run simulation

Storage system variables - Single run

Auxiliary loads	kW	(0.2 - 2)	<input type="text" value="0.7"/>	Inert weight fraction	-	(0 - 0.4)	<input type="text" value="0.1"/>
Combustor efficiency	-	(0.5 - 1)	<input type="text" value="0.9"/>	Refueling fraction	-	(0.5 - 1)	<input type="text" value="0.85"/>
Extra volume	L	(0 - 200)	<input type="text" value="0"/>	Refueling pressure	bar	(60 - 110)	<input type="text" value="100"/>
Hydr. crystal density	kg/m ³	(500 - 7000)	<input type="text" value="851.41"/>	Refueling temperature	C	(-20 - 50)	<input type="text" value="39.7"/>
Hydr. weight fraction	-	(0.01 - 0.2)	<input type="text" value="0.11"/>				
Hydride mass	kg	(1 - 400)	<input type="text" value="66"/>				
Hydride void fraction	-	(0.2 - 0.6)	<input type="text" value="0.3"/>				

Inputs

Results (at end of simulation)

H2 delivered	kg	<input type="text" value="5.83906"/>
H2 used	kg	<input type="text" value="5.84208"/>
Gravimetric capacity	%	<input type="text" value="5.65717"/>
Volumetric capacity	g/L	<input type="text" value="40.5111"/>
Temperature	C	<input type="text" value="70.9497"/>
Pressure	bar	<input type="text" value="5.00862"/>
Fuel economy	mpgge	<input type="text" value="49.4854"/>
Range	miles	<input type="text" value="286.948"/>
Distance traveled	miles	<input type="text" value="430.386"/>

Stop simulation

Save results

Generate all plots

Save results and generate Matlab® plots

Pressure [bar]

time [s]

Zoomable plots

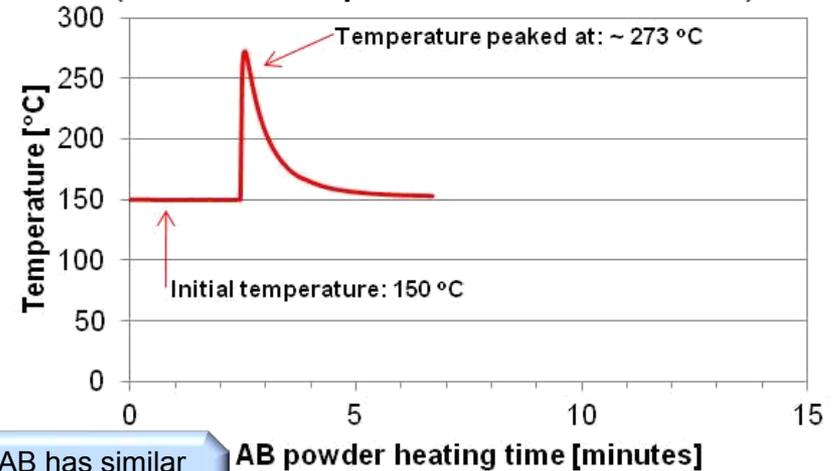
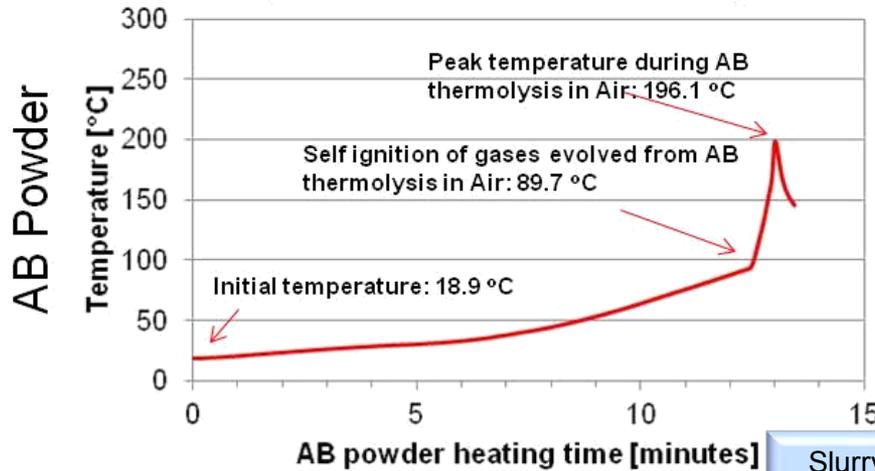
In beta test with ORNL and SNL.

Risk Assessment

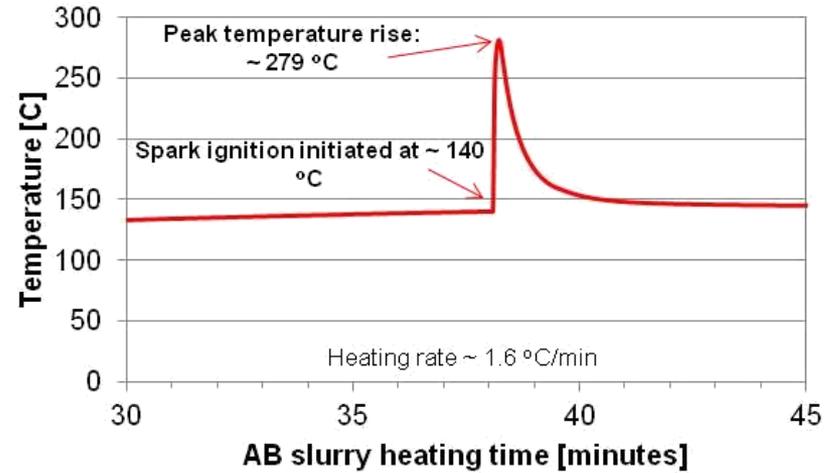
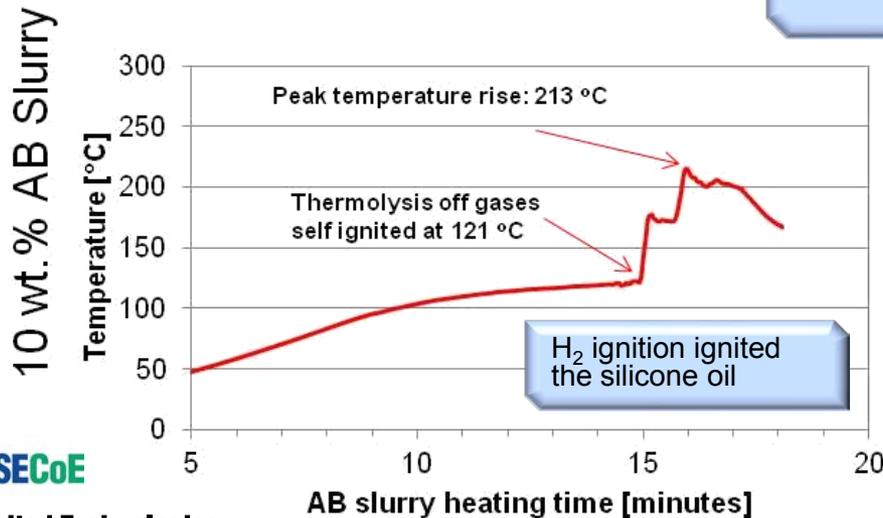
(Comparison of solid AB versus liquid AB in terms of flammability)

AB thermolysis in open air
(inside ventilated hood)

AB thermolysis in enclosed air
(8.3 liters spherical test vessel)



Slurry AB has similar ignition properties as solid AB.



Particulates

(SAE J2719 April 2008 Hydrogen Quality Guideline for FCV)

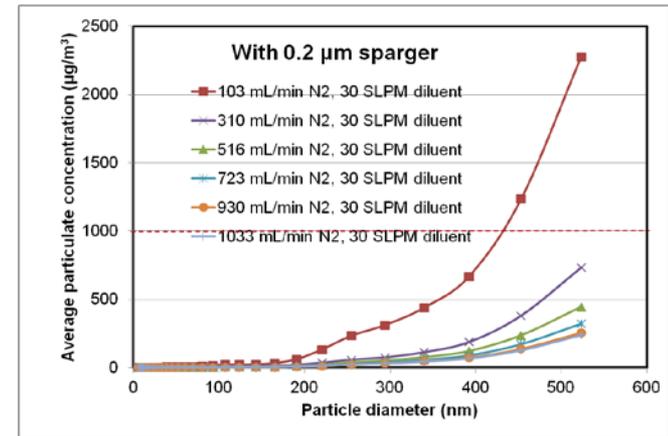
Contaminant	ppm		
Water	5	Particulate size	<10 μ m
Total hydrocarbons (C1 basis)	2	Particulates	<1 μ g/L
Oxygen	5		
Helium	300		
Inert gases (N2, Ar)	100		
Carbon dioxide	2		
Carbon monoxide	0.2		
Sulfur compounds	0.004		
Formaldehyde	0.01		
Formic acid	0.2		
Ammonia	0.1		
Total halogenates	0.05		
Total gases *	300		
Hydrogen fuel index (minimum, %)	>99.97		



- Porous stainless steel filters tested with MOF-5 and Maxsorb



- Initial results show that MOF-5 particulate concentration is below SAE guideline but there are measurement system limitations



Engine Exhaust Particle Sizer™ Spectrometer

- Need to collect data at higher flow rates to simulate flow-through cooling

* The value of total gases is the summation of the values of impurities listed in this table

FY12 and FY13 Plan

(Contingent on Phase 2 to Phase 3 transition and budget)

Task	Description	FY13				FY14	
		1Q	2Q	3Q	4Q	1Q	2Q
Project Management	Go/No-Go meeting Phase 2 to Phase 3 transition			★			
	F2F-meetings; Tech Team Review; Annual Merit Review	■		■	■	■	■
	Quarterly Financial and Technical Reports	●		●	●	●	●
Chemical Hydride Operability	Validate gas-liquid separator model		■				
	Optimize gas-liquid separator internals			■			
	Use tools to design gas-liquid separator for Phase 3			■			
	Determine integration opportunities of gas-liquid separator with other components.				■		
H2 Quality	Fabricate filter material for Phase 3 at sub-scale prototype level.			■			
	Fabricate filter housing.				■		
	Demonstrate H2 Quality targets in Phase 3.				■		
	Mitigate any Phase 3 operability issues				■		
IPPSSM	Lead IPPSSM Technical Area (TA)	■					
	Support Model Integration	■					
	Maintain Vehicle/Storage System Framework	■					
	Update models with Phase 3 sub-scale prototype findings				■		
	Provide input and support sub-scale prototype testing in Phase 3.			■			
Risk Assessment	Assess risks of chemical hydride system.			■			
	Assess risks of adsorbent system.			■			

Summary

Relevance: Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles.

Approach: Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H₂ storage for automotive applications.

Technical Accomplishments and Progress:

- Demonstrated Gas/Liquid Separator (GLS) S*M*A*R*T milestone with surrogate material.
- Determined operating characteristics of GLS system.
- Developed GLS model as design tool.
- Demonstrated regenerable NH₃ filter S*M*A*R*T milestone by minimizing weight and volume for 1800 miles regeneration interval.
- Developed and validated NH₃ filter dynamic sorption model.
- IPPSSM: Developed graphical user interface (GUI) and performed beta test. Supported integration of H₂ storage models into framework.
- Determined that slurry AB has similar ignition properties as solid AB.
- Collaborated with BASF/Ford on risk assessment of MOF-5.
- Tested performance of SS particulate filters with MOF-5 and MaxSorb.

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy under Contract No. DE-FC36-09GO19006.

The authors would like to thank all members of the HSECoE for stimulating discussions, Richard Chahine for providing IRH-33 and Jesse Adams, Bob Bowman and Ned Stetson for their outstanding support.

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Questions and suggestions?



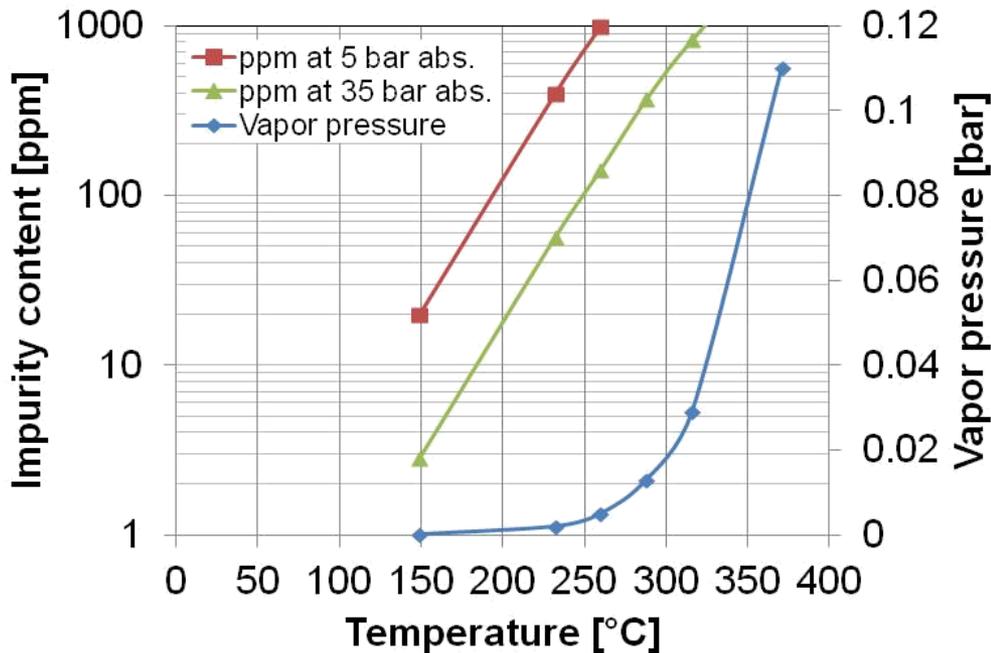
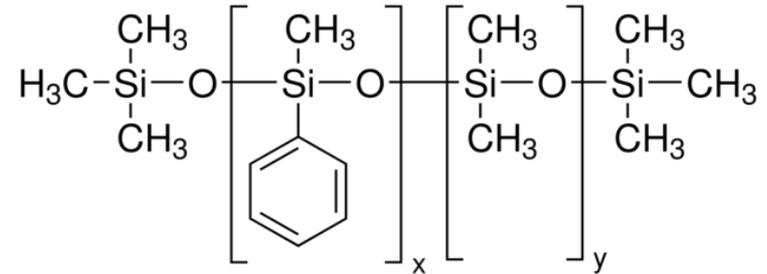
Technical Back-Up Slides

Publications and presentations

- Bart A. van Hassel, Mikhail Gorbounov, John Holowczak, Igor Fedchenia, Xia Tang, and Ron Brown, “Advancement of System Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage”, MH2012 invited paper, accepted by Journal of Alloys and Compounds.
- 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*.
- Bart A. van Hassel, Daniel A. Mosher, José Miguel Pasini, Mikhail Gorbounov, John Holowczak, Xia Tang, Robert Brown, Bruce Laube, and Lawrence Pryor, “Engineering improvement of NaAlH₄ system,” *Int. J. Hydrogen Energy* **37**, 2756–2766 (2012).
- José Miguel Pasini, Bart A. van Hassel, Daniel A. Mosher and Michael J. Veenstra, “System modeling methodology and analyses for materials-based hydrogen storage,” *Int. J. Hydrogen Energy* **37**, 2874–2884 (2012).
- Matthew Thornton, Jon Cosgrove, Aaron Brooker, José Miguel Pasini, and Michael J. Veenstra, “Development of a vehicle level simulation model for evaluating the trade-off between various advanced on-board hydrogen storage technologies for fuel cell vehicles,” SAE Technical Paper 2012-01-1227, *SAE 2012 World Congress & Exhibition*, April 2012, Detroit, MI, USA (2012).
- Bart A. van Hassel, Engineering progress in materials based H₂ storage for light-duty vehicles, IEA Task 22, May 10, 2012
- Bart A. van Hassel, Engineering Aspects of Materials Based Hydrogen Storage Systems, IEA Task 32, October 26-27, 2012.

Impurities introduced by liquid media

- Product name: Silicone oil AP 100
- Viscosity: ~100 mPa.s at 25°C

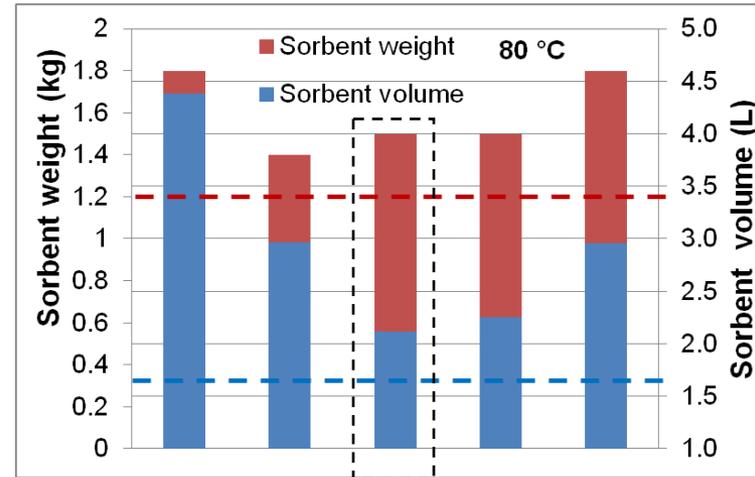
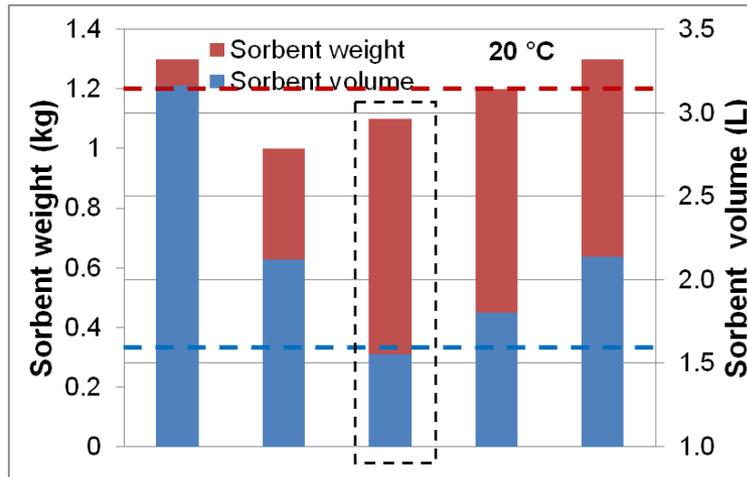


Dow Corning
710 Fluid

Temperature control
required to prevent
degradation, e.g. <260°C

Weight and Volume of Full Scale Ammonia Filter

1800 miles/ exchange, 60 miles/kg H₂, NH₃ concentration 500 ppm



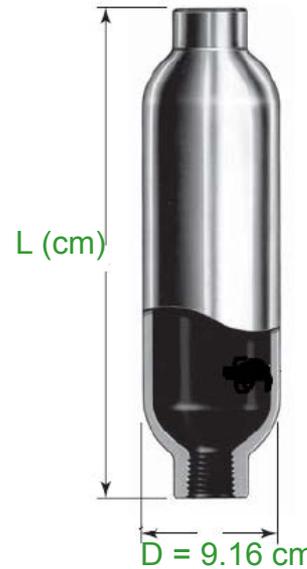
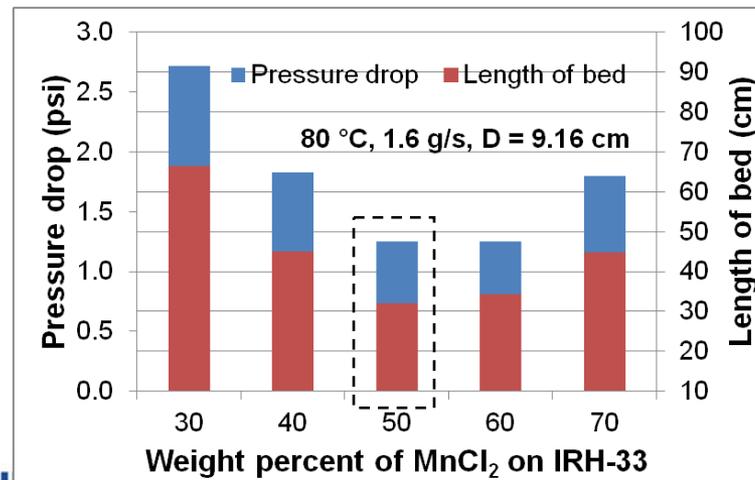
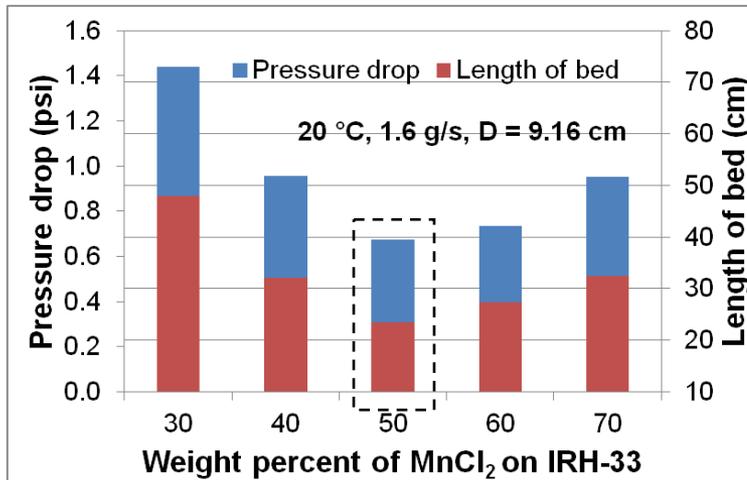
Weight percent of MnCl ₂ on IRH-33	30	40	50	60	70
Density (g/cc)	0.411	0.472	0.709	0.665	0.609
NH ₃ dynamic adsorption capacities (wt%)	9.62	12.52	11.25	10.67	9.64

Weight percent of MnCl ₂ on IRH-33	30	40	50	60	70
Density (g/cc)	0.411	0.472	0.709	0.665	0.609
NH ₃ dynamic adsorption capacities (wt%)	6.9	9.09	8.71	8.51	6.9

Ammonia Filter with 50 wt% MnCl₂ on IRH-33 meets weight and volume targets of HSECoE

Pressure Drop and Size

1800 miles/ exchange, 60 miles/kg H₂, NH₃ concentration 500 ppm
 Absolute Pressure of hydrogen gas - 5 bar



Darcy's Law: $\Delta P = \frac{Q\mu L}{KA}$

$K = 2.4 \times 10^{-10} - 2.8 \times 10^{-10} \text{ m}^2$
 (Estimated from experiments)

Porosity = 30%

Average particle diameter = 800 μm

Ammonia Filter with 50 wt% MnCl₂ on IRH-33 shows the lowest pressure drop and the smallest column length



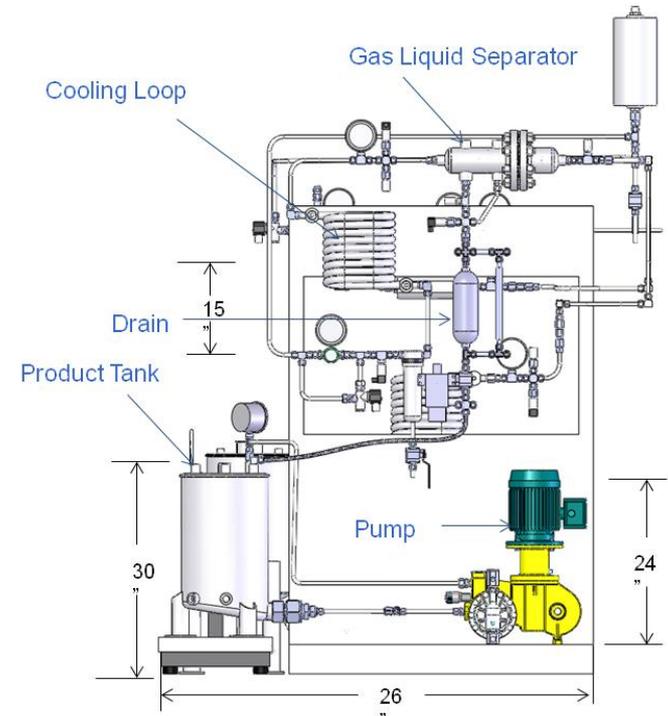
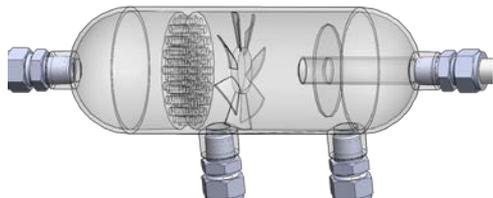
Past Status

- Beginning of Phase 2 (03/31/2011):
 - Transitioned from solid AB to AB in a fluid form (liquid or slurry).
 - NH_3 sorbent with 5 wt% dynamic sorption capacity.

- Last Tech Team Review (02/15/2012):
 - Designed a gas-liquid separator test facility.
 - Selected custom designed static gas-liquid separator (GLS).

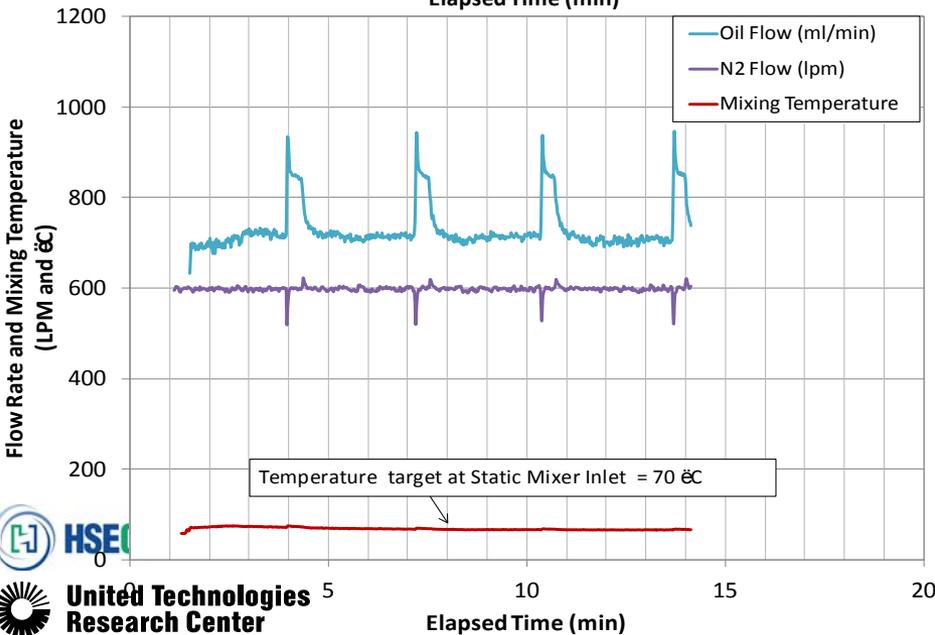
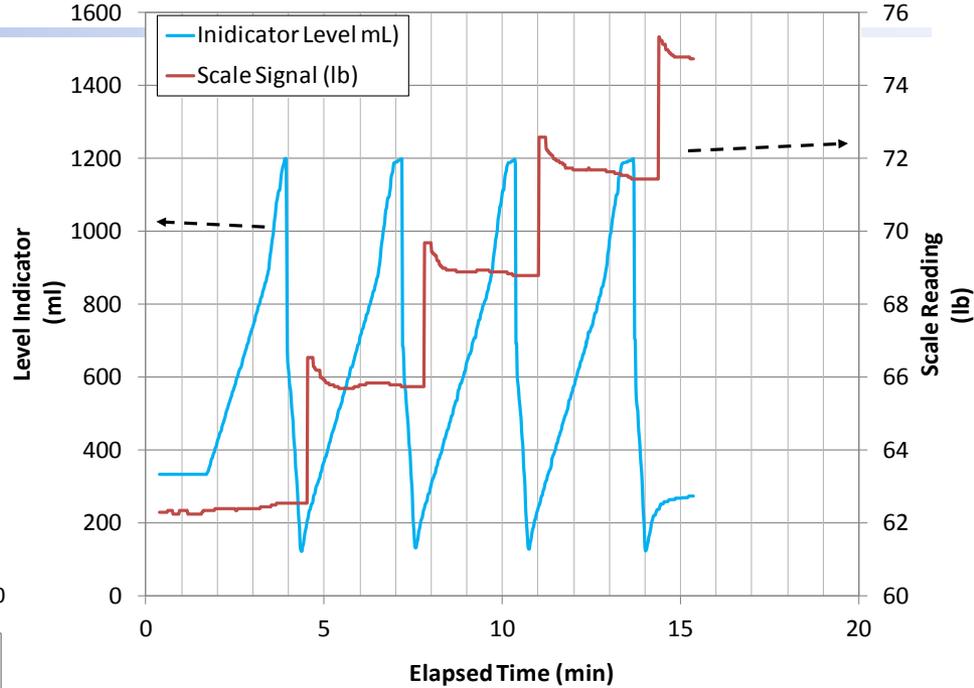
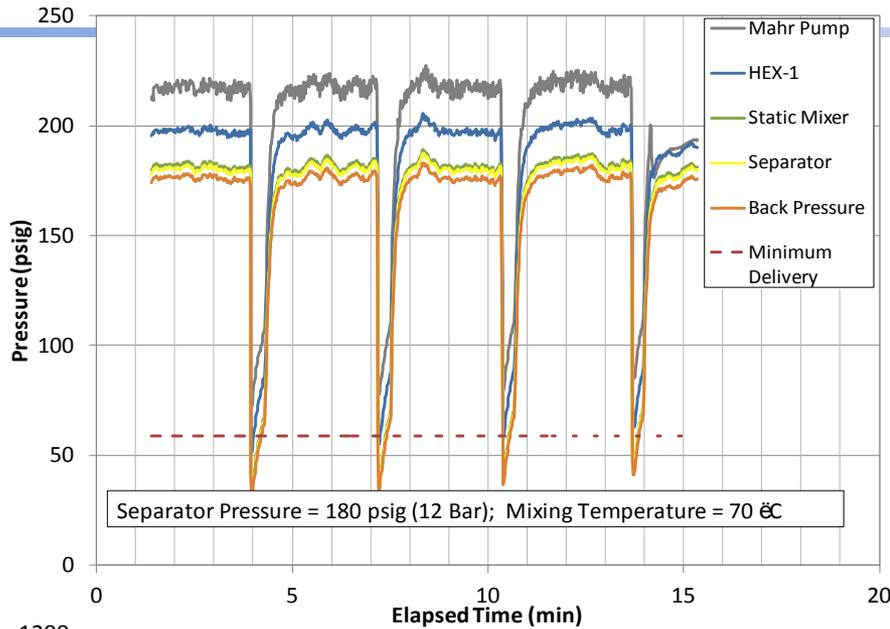


Flexible screw auger



- Reported high dynamic sorption capacity NH_3 sorbent (11 wt%).

GLS system operating characteristics



S*M*A*R*T Milestone Conditions:
 Silicone Oil AR 20 Flow = 720 ml/min
 N2 Flow = 600 slpm
 Mixing Temperature = 70°C
 System Pressure ~ 180 psig (12 Bar)
 Separation Efficiency = (99.92±0.02)% n=3