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**

Pacific Northwest NATIONAL LABORATORY

SRNL SAVANNAH RIVER NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY

LINCOLN COMPOSITES A Member of Hexagon Composites Group

HRI UQTR UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES

GM

Ford

BASF The Chemical Company

OSU Oregon State UNIVERSITY

JPL

CALIFORNIA INSTITUTE OF TECHNOLOGY 1891

NREL National Renewable Energy Laboratory Innovation for Our Energy Future

HSECoE

IEA HIA Task 32

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* DOE EERE HFCIT Program Multi-year Plan for Storage

Objectives

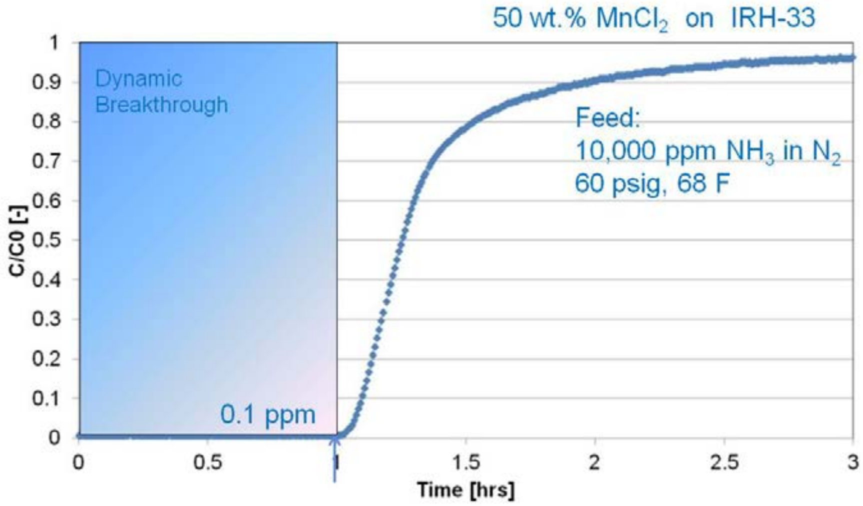
- Design of materials-based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles.

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
  - H_2 quality (NH_3 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
- H_2 quality:
  - Collected experience data from partners about particulate mitigation in flow through cryo-adsorbent systems
  - Developed NH_3 filter and provided filters for testing at LANL in combination with other impurities (competitive adsorption with borazine)
  - Developed NH_3 sorbent filter model and validated model
- Simulink® Framework:
  - Developed graphical user interface (GUI) architecture and performed beta-test
  - Compared H_2 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

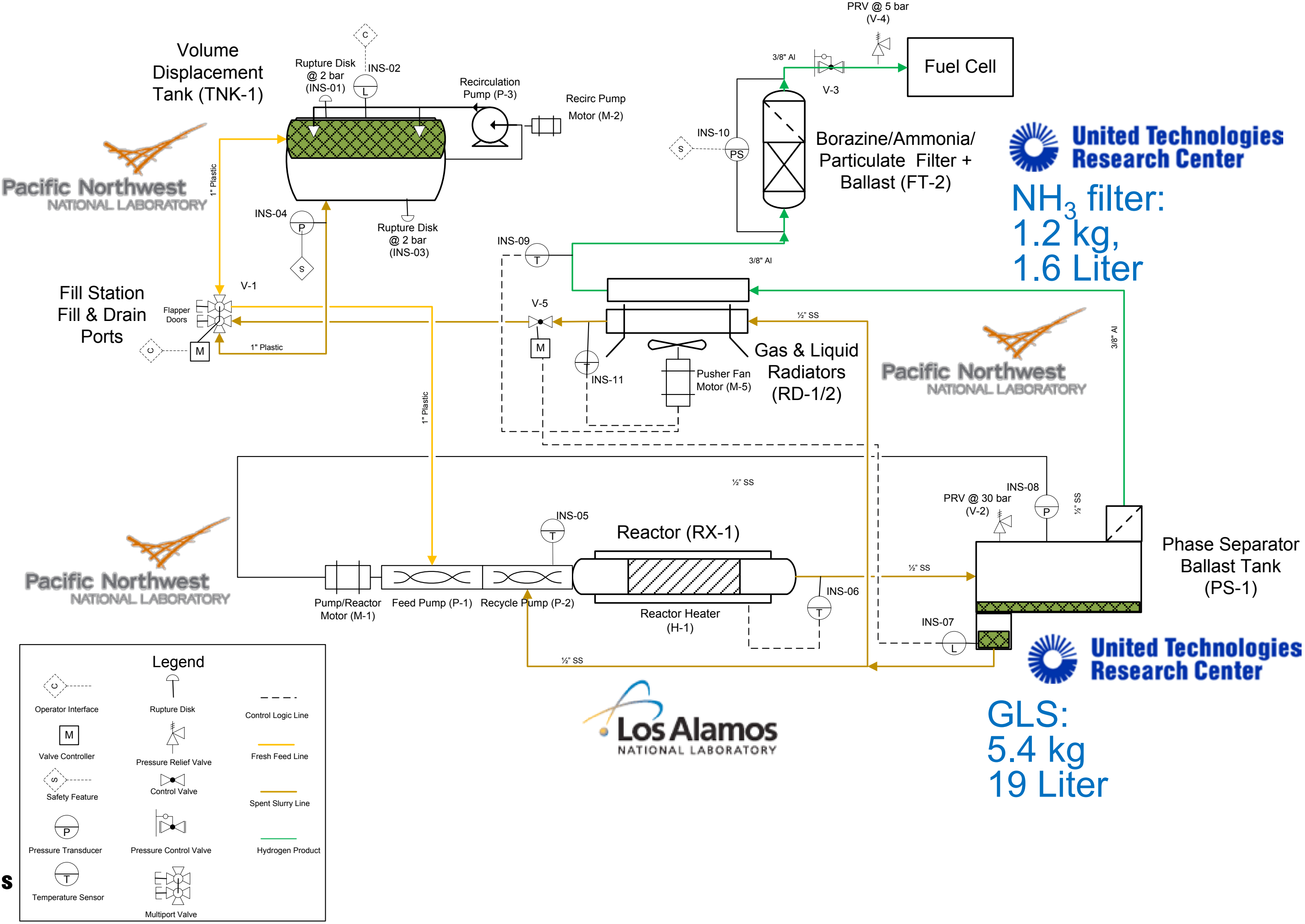
Use results to estimate material property requirement for DOE’s 2017 system level targets.

Collaborations

United Technologies Research Center HRI UQTR GM BASF The Chemical Company Ford	- MOF-5 risk assessment - Particulate mitigation
United Technologies Research Center Pacific Northwest NATIONAL LABORATORY HRI UQTR Los Alamos NATIONAL LABORATORY EST. 1943	- 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
United Technologies Research Center Ford NREL National Renewable Energy Laboratory Innovation for Our Energy Future SRNL SAVANNAH RIVER NATIONAL LABORATORY Pacific Northwest NATIONAL LABORATORY	- 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



NH$_3$ filter:
1.2 kg,
1.6 Liter

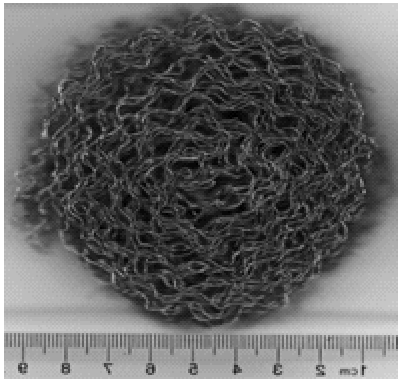
GLS:
5.4 kg
19 Liter

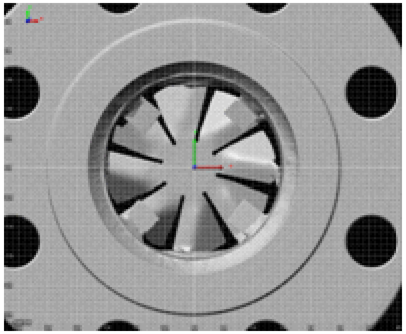
Gas Liquid Separation for Chemical Hydrides

- GLS design features:

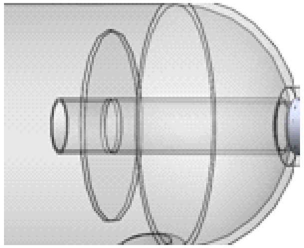
Demister pad

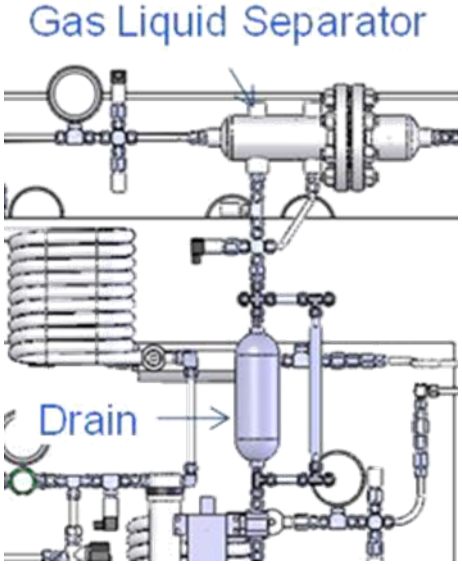
Static vane pack induces a swirl





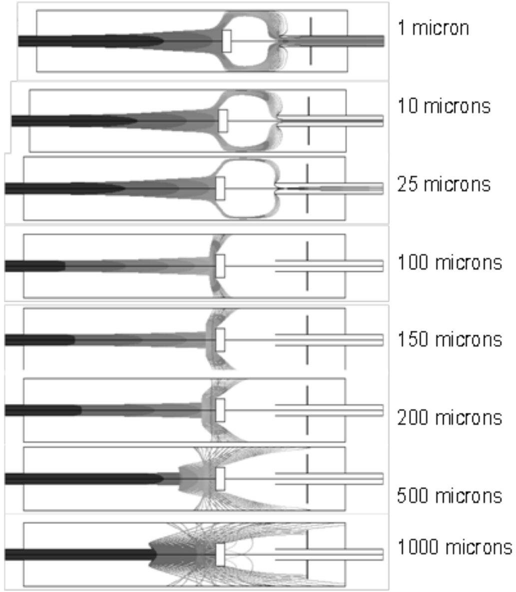
Vortex finder





Surrogate spent fuel reservoir with drain and level control

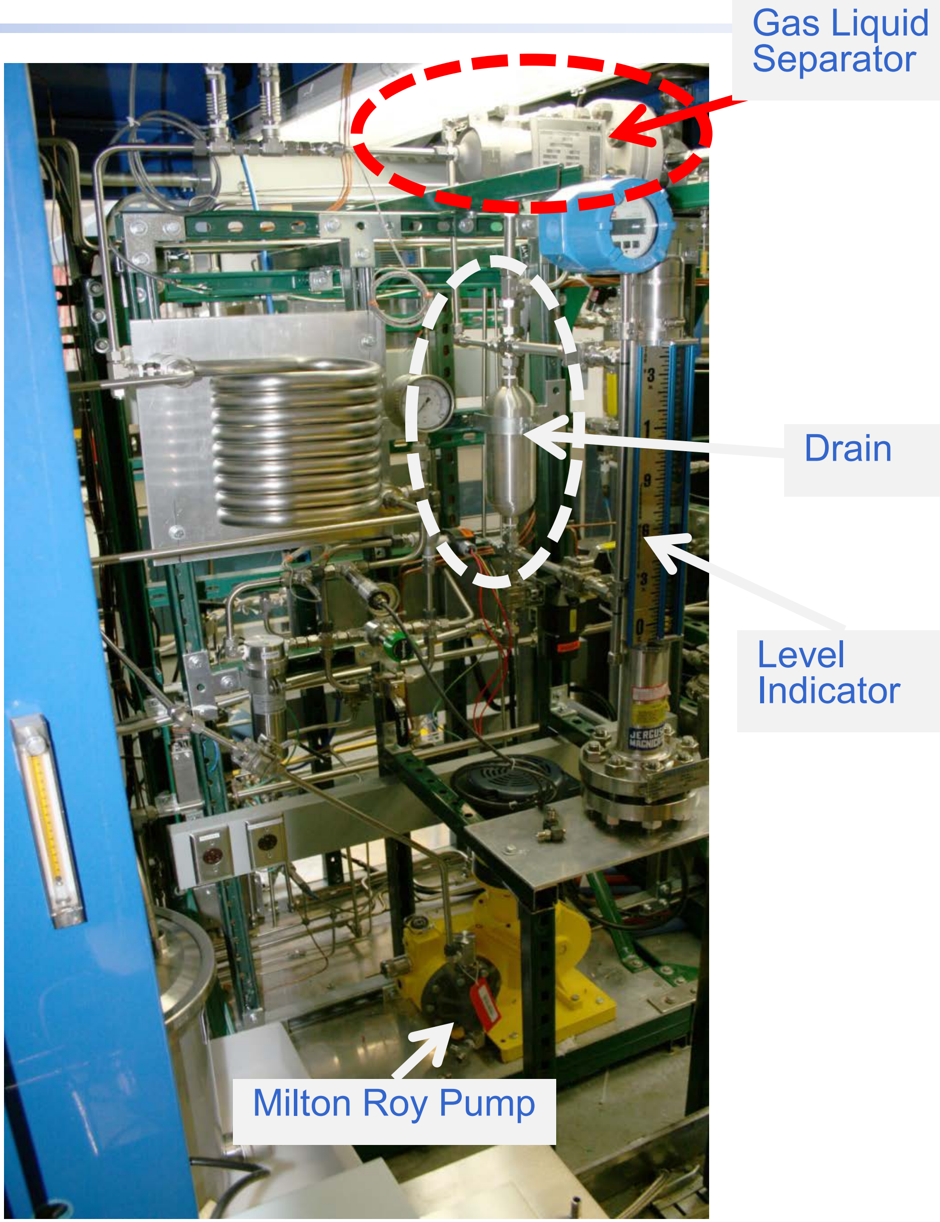
- Droplet transport model developed in order to improve GLS design



Validate model with droplet size distribution measurement in outlet

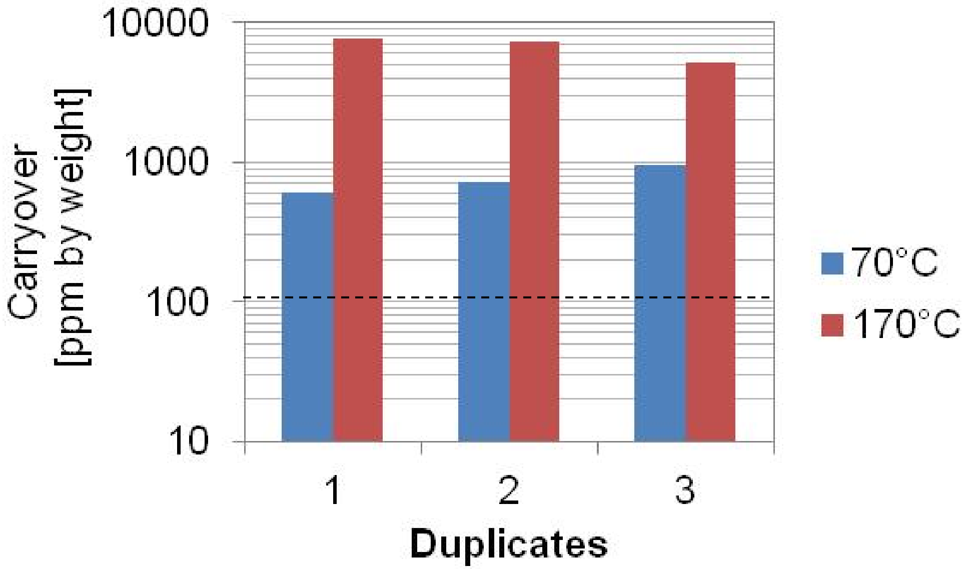
Gas Liquid Separator (GLS) Test Facility at UTRC

- Constructed gas-liquid separator test facility
- Completed test facility shake down:
  - N_2 as surrogate for H_2
  - 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



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 H_2 @ STP (40 wt% AB @ 2.35 Eq H_2 and max H_2 flow of 0.8 g/s H_2) … 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	$(8\pm2)*10^2$
170	7808	7189	5192	$(7\pm1)*10^3$

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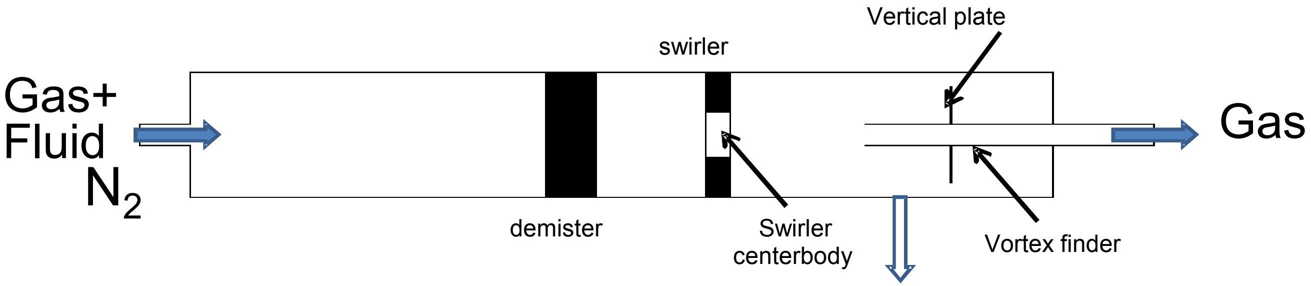
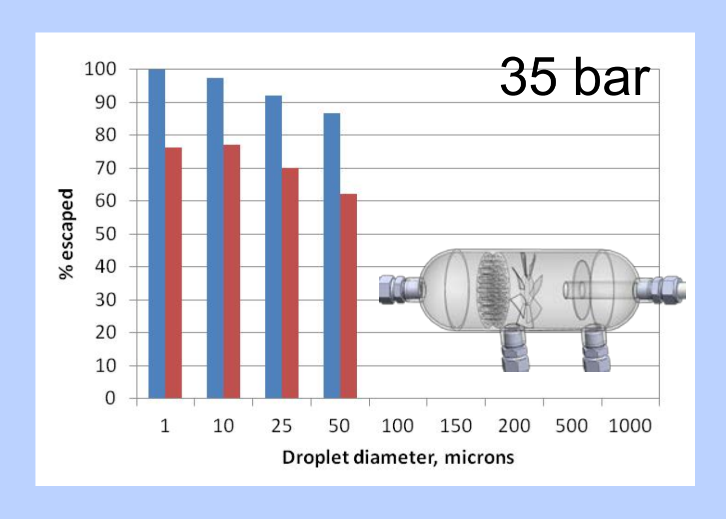
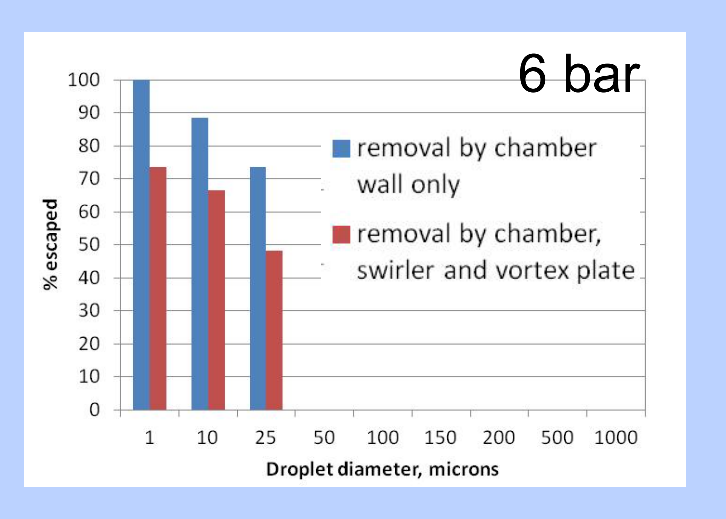
GLS Model Development

- 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



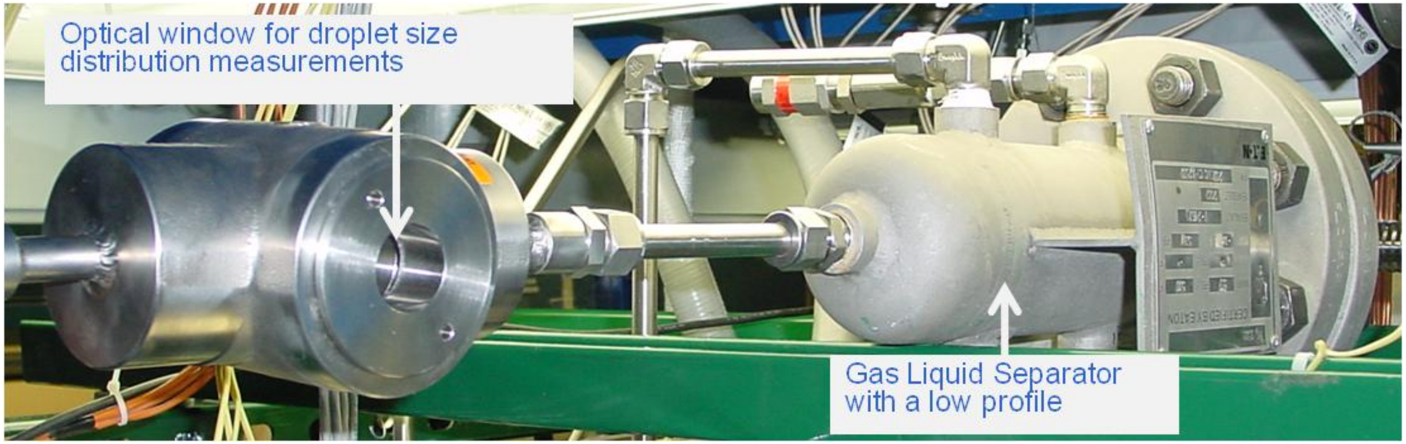


- Determined need for coalescence filter to remove small droplets

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:

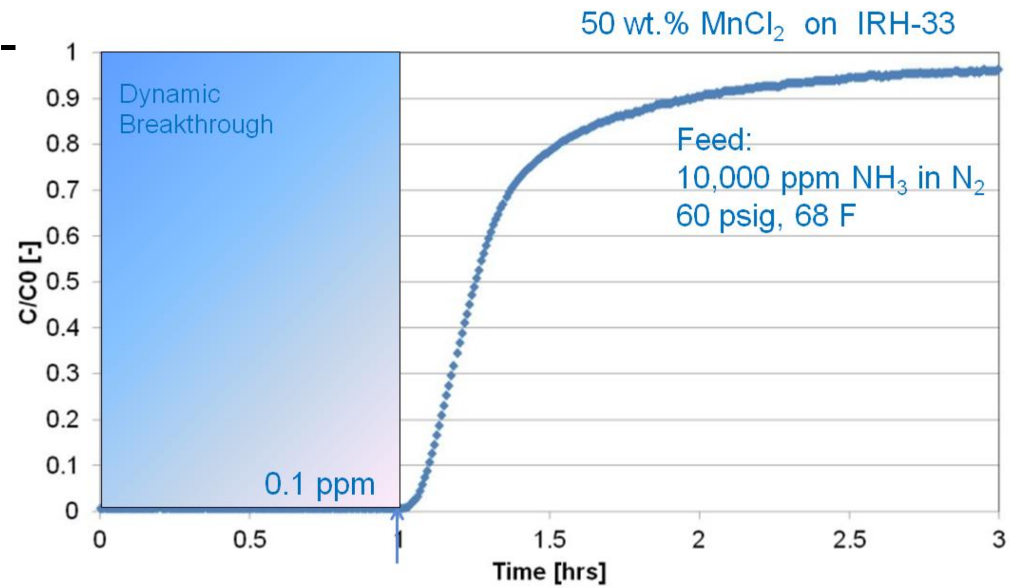


- Developed capability to design gas-liquid separator for Phase 3
- Identified drain and level control system as opportunities for integration with gas-liquid separator in order to reduce weight and volume
- Recommended further integration between thermolysis reactor and gas-liquid separator

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

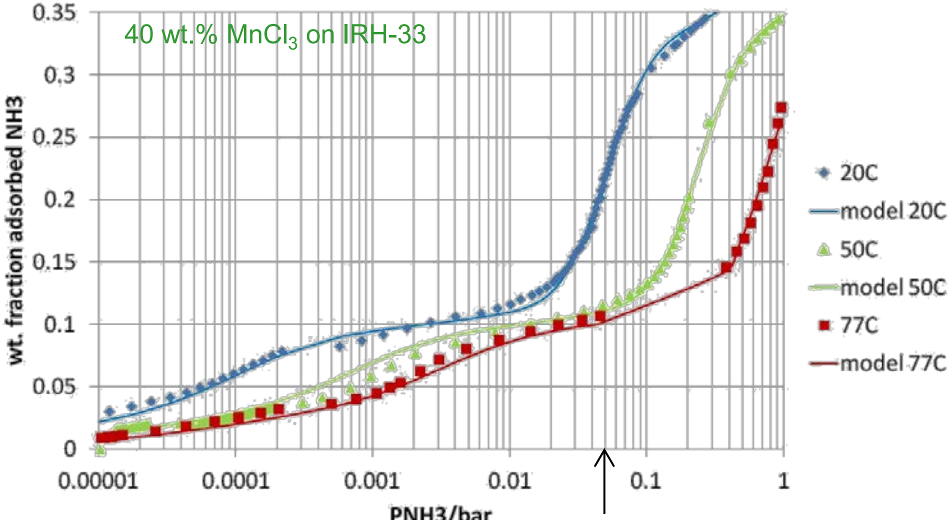


- Apply learning from evaluating particulate filters for cryo-adsorption system (<10μm, <1 μg/L)

NH_3 Sorbent Filter Results

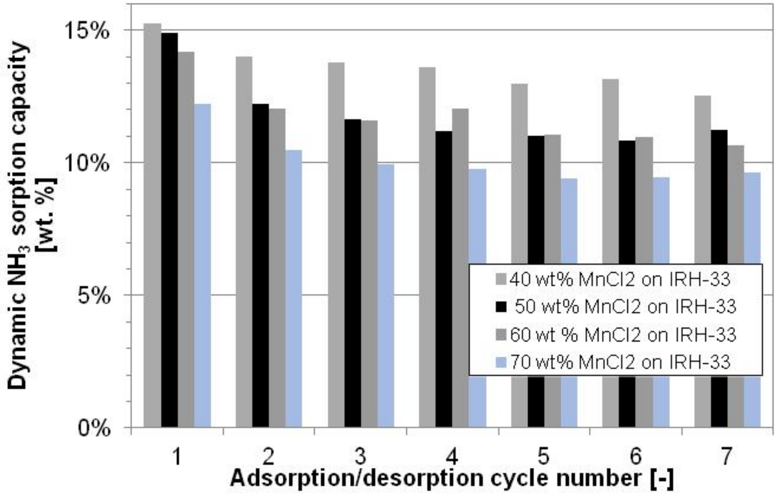
- Demonstrated S*M*A*R*T milestone of NH_3 filter:
  - …Ammonia scrubber with a minimum replacement interval of 1800 miles… outlet concentration of 0.1 ppm (inlet concentration = 500 ppm) …..< 1.2 kg and < 1.6 liter…..

- Characterized NH_3 adsorption isotherm (-20, 0, 20, 50, 77°C)



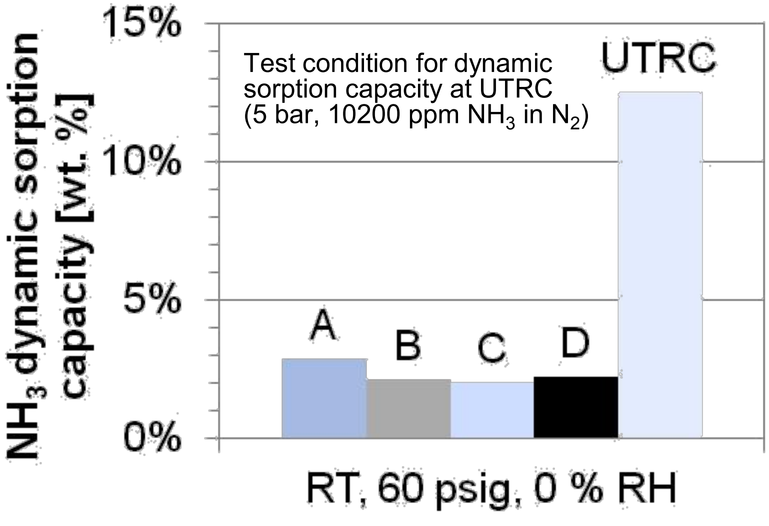
Test condition for dynamic sorption capacity at UTRC
(5 bar, 10200 ppm NH_3 in N_2)

- Optimized capacity and demonstrated sorbent regeneration



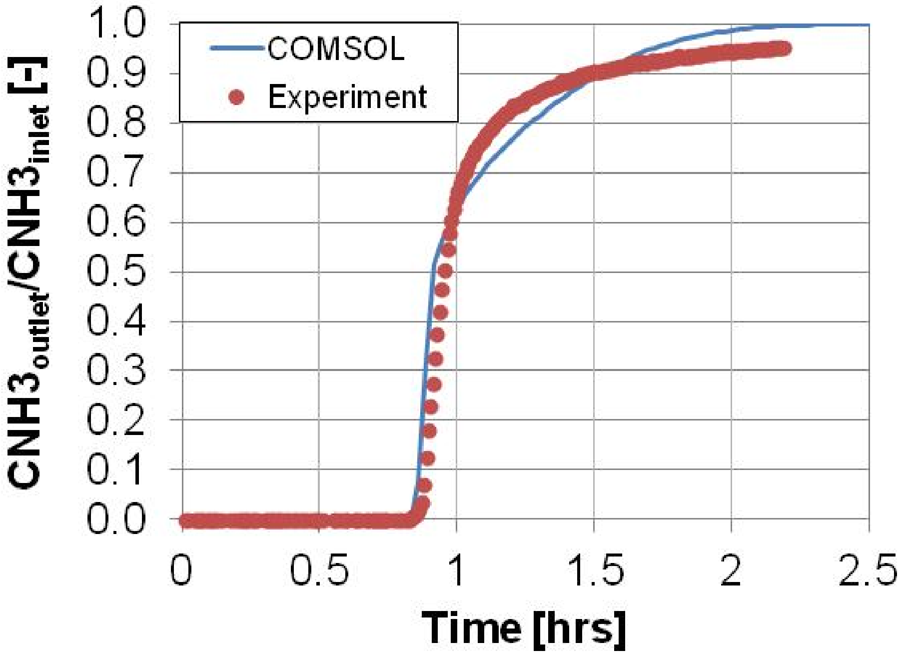
Dynamic NH_3 Sorption Capacity

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



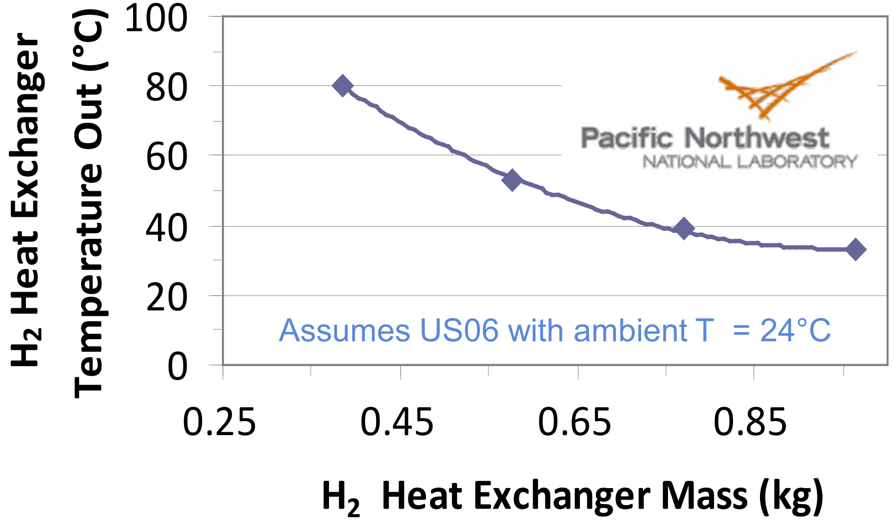
Ammonia Filter with 50 wt% $MnCl_2$ on IRH-33 meets weight and volume targets of HSECoE

- Developed and validated dynamic adsorption breakthrough model

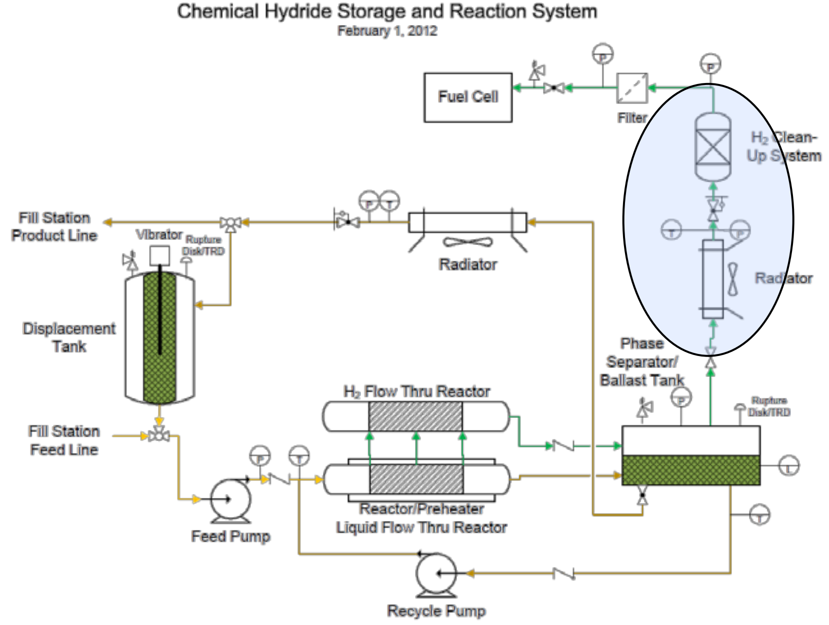


Demonstrated that ammonia can be adsorbed to produce fuel-cell grade hydrogen

Minimizing NH_3 filter and H_2 gas cooler weight



Assumes US06 with ambient T = 24°C

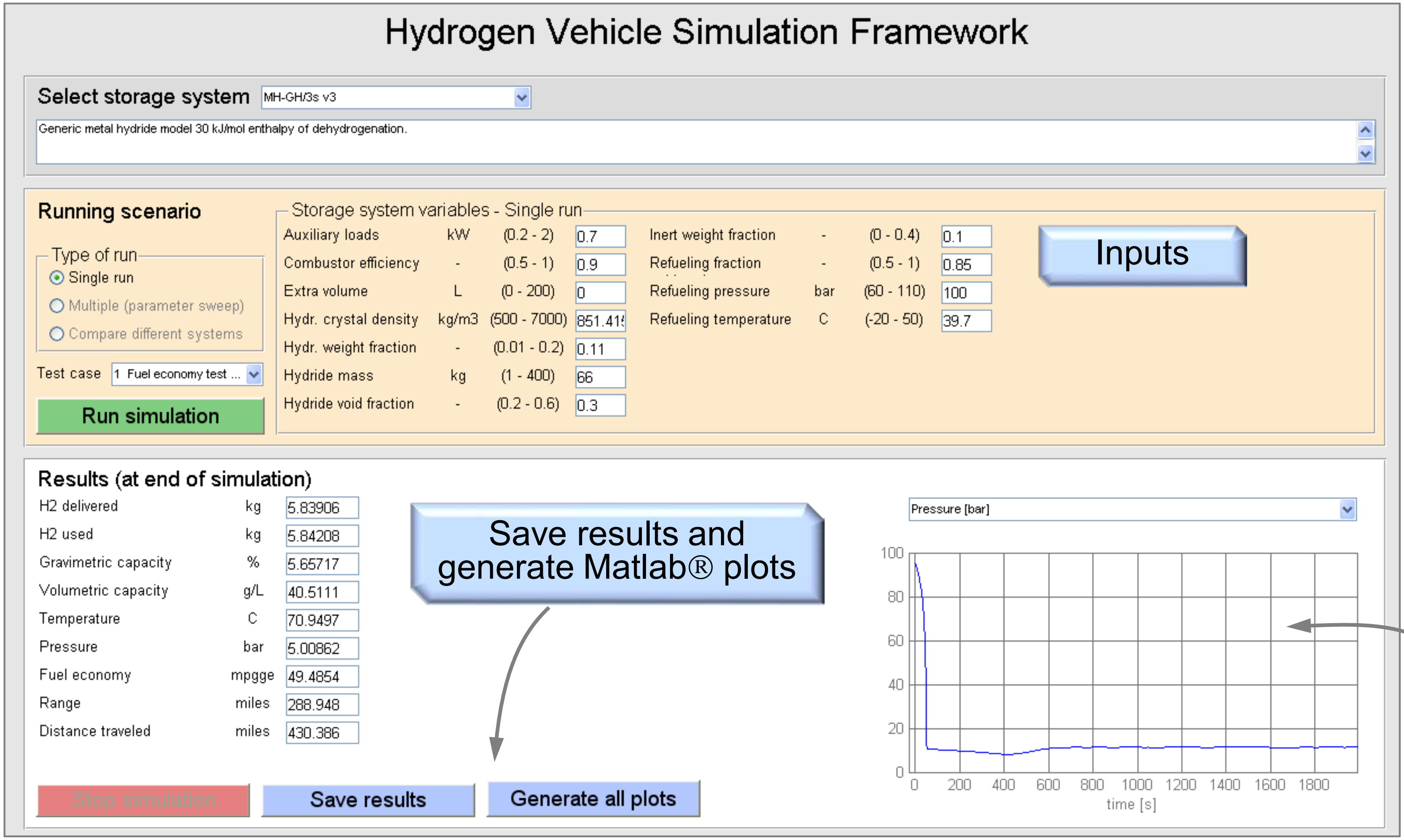


Radiator outlet temperature or Inlet temperature of adsorbent bed (°C)	Heat exchanger weight (kg)	Dynamic NH_3 sorption capacity (wt%)	NH_3 filter weight (kg)	Total weight (filter + Heat exchanger) (kg)
23	0.965	11.25	1.1	2.07
50	0.577	9.31	1.3	1.88
80	0.385	8.71	1.5	1.86

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



Select storage system: MH-GH/3s 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 ...

Storage system variables - Single run

Auxiliary loads	kW	(0.2 - 2)	0.7
Combustor efficiency	-	(0.5 - 1)	0.9
Extra volume	L	(0 - 200)	0
Hydr. crystal density	kg/m3	(500 - 7000)	851.41
Hydr. weight fraction	-	(0.01 - 0.2)	0.11
Hydride mass	kg	(1 - 400)	66
Hydride void fraction	-	(0.2 - 0.6)	0.3
Inert weight fraction	-	(0 - 0.4)	0.1
Refueling fraction	-	(0.5 - 1)	0.85
Refueling pressure	bar	(60 - 110)	100
Refueling temperature	C	(-20 - 50)	39.7

Inputs

Results (at end of simulation)

H2 delivered	kg	5.83906
H2 used	kg	5.84208
Gravimetric capacity	%	5.65717
Volumetric capacity	g/L	40.5111
Temperature	C	70.9497
Pressure	bar	5.00862
Fuel economy	mpgge	49.4854
Range	miles	288.948
Distance traveled	miles	430.386

Save results and generate Matlab® plots

Pressure [bar]

Zoomable plots

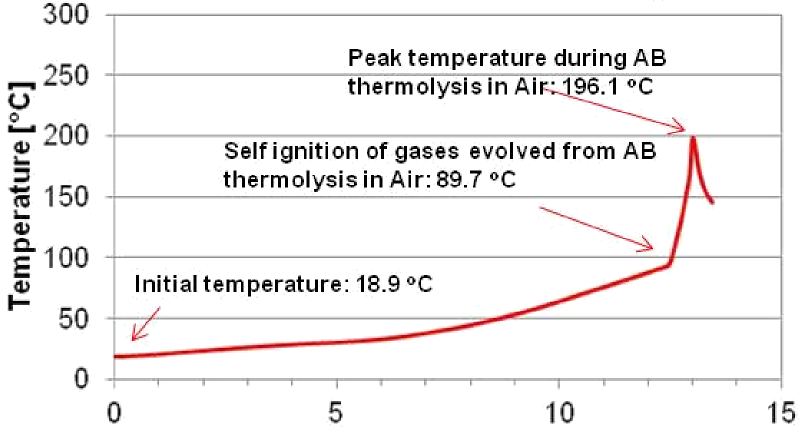
In beta test with ORNL and SNL.

Risk Assessment

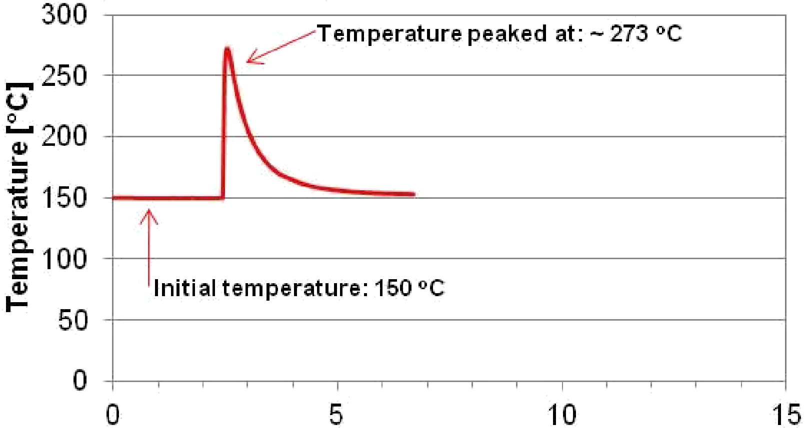
(Comparison of solid AB versus liquid AB in terms of flammability)

AB Powder

AB thermolysis in open air
(inside ventilated hood)

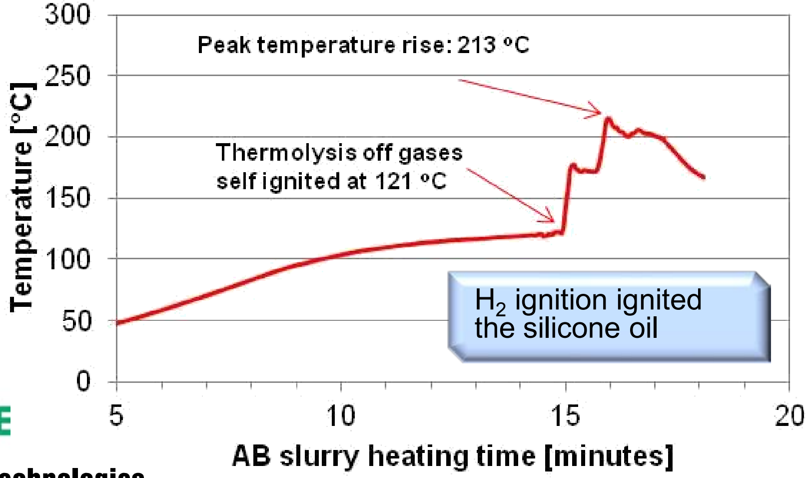


AB thermolysis in enclosed air
(8.3 liters spherical test vessel)

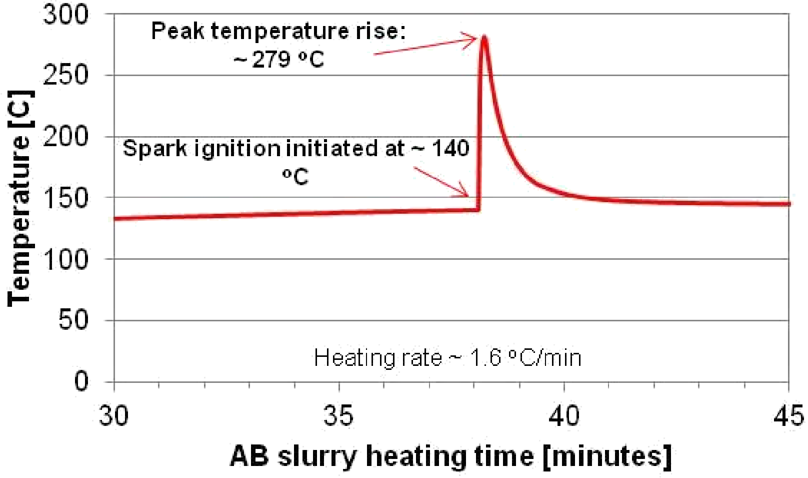


Slurry AB has similar ignition properties as solid AB.

10 wt. % AB Slurry



H_2 ignition ignited the silicone oil



Particulates

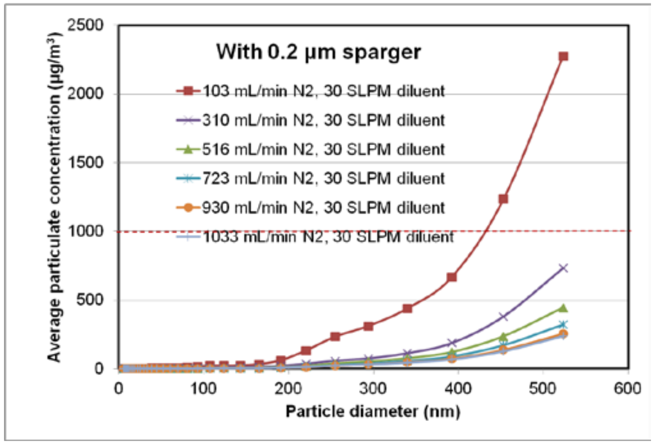
(SAE J2719 April 2008 Hydrogen Quality Guideline for FCV)

Contaminant	**ppm**		
Water	5	Particulate size	<10µm
Total hydrocarbons (C1 basis)	2	Particulates	<1µg/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		

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

- 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

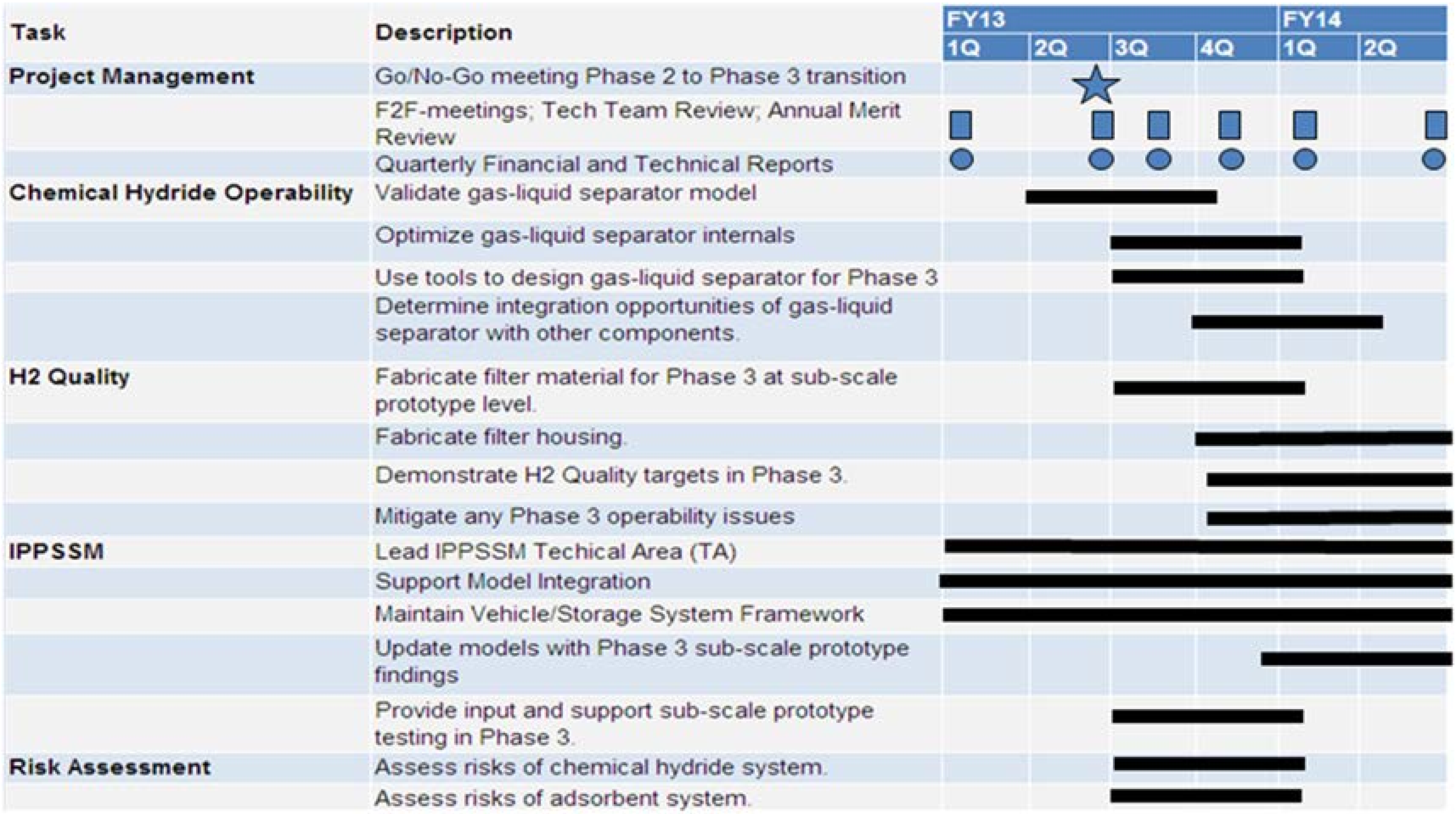


Engine Exhaust Particle Sizer^{TM} Spectrometer

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

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 Techical 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.			▬	▬		

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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 H_2 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 NH_3 filter S*M*A*R*T milestone by minimizing weight and volume for 1800 miles regeneration interval.
- Developed and validated NH_3 filter dynamic sorption model.
- IPPSSM: Developed graphical user interface (GUI) and performed beta test. Supported integration of H_2 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.

Questions and suggestions?

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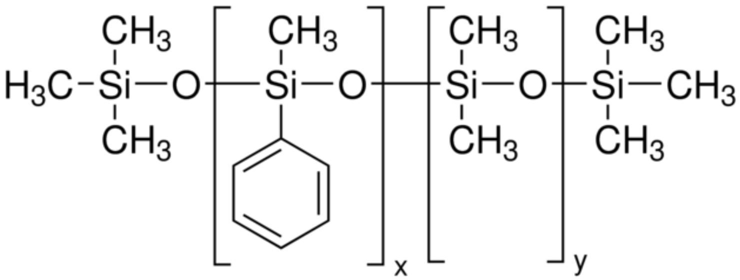
Technical Back-Up Slides

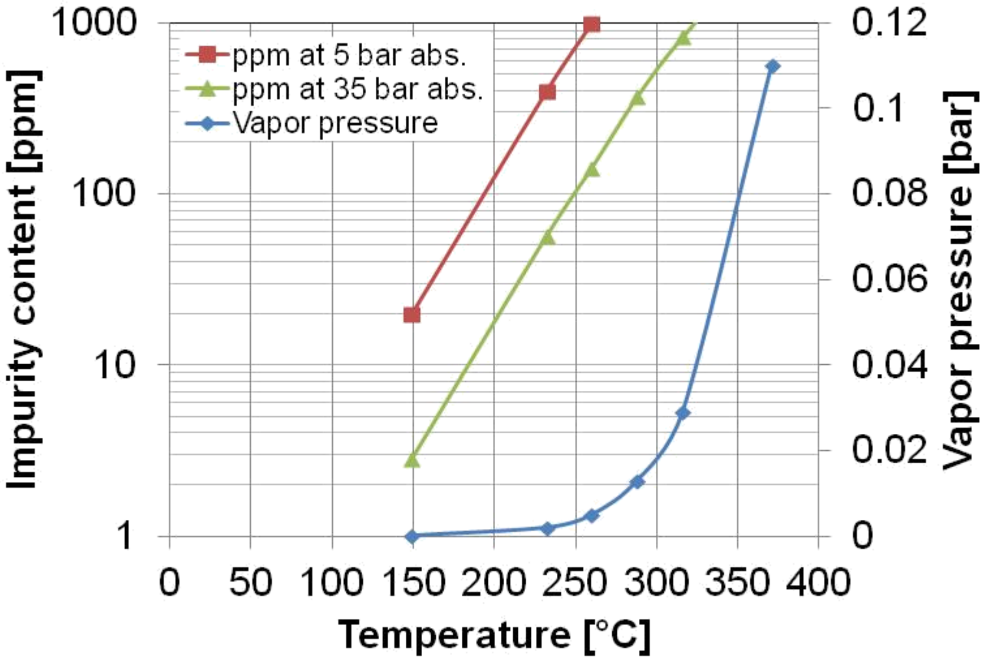
Publications and presentations

- 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 $NaAlH_4$ 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 H_2 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

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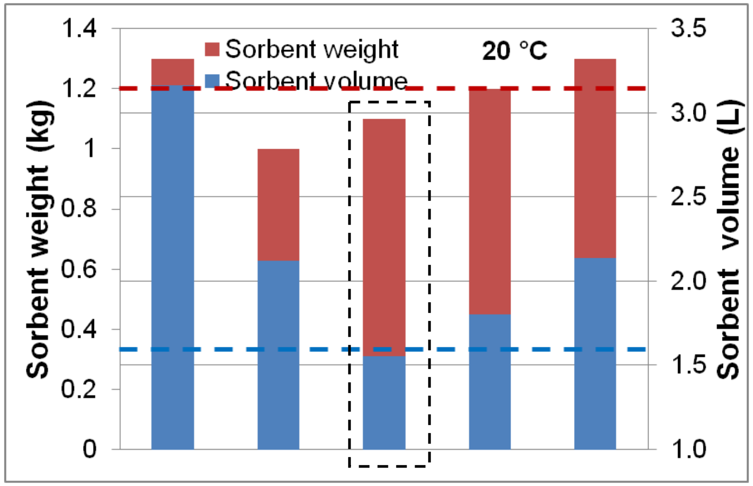
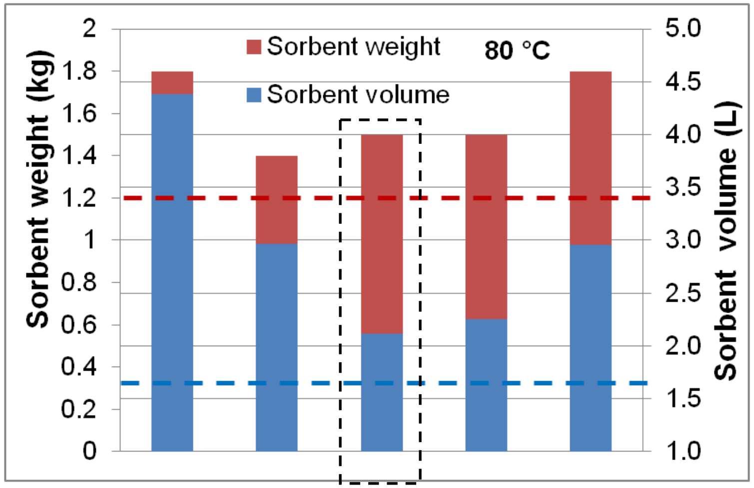
Weight and Volume of Full Scale Ammonia Filter

1800 miles/ exchange, 60 miles/kg H_2, NH_3 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
NH3 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
NH3 dynamic adsorption capacities (wt%)	6.9	9.09	8.71	8.51	6.9

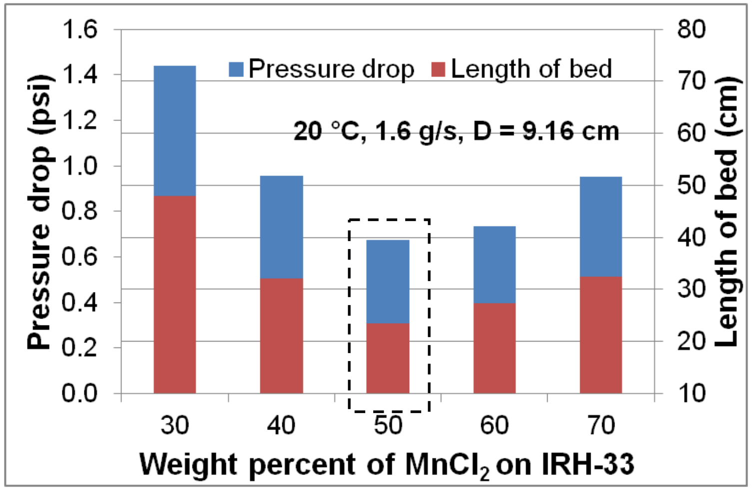
Ammonia Filter with 50 wt% $MnCl_2$ on IRH-33 meets weight and volume targets of HSECoE

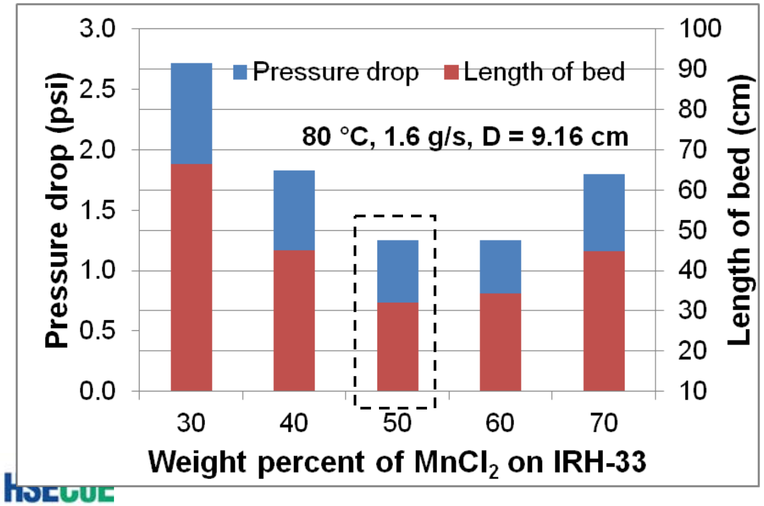
HSECoE

United Technologies
Research Center

Pressure Drop and Size

1800 miles/ exchange, 60 miles/kg H_2, NH_3 concentration 500 ppm
Absolute Pressure of hydrogen gas - 5 bar





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

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

Porosity = 30%
Average particle diameter = 800 μm

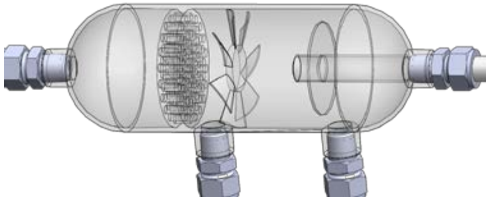
Ammonia Filter with 50 wt% $MnCl_2$ on IRH-33 shows the lowest pressure drop and the smallest column length

Past Status

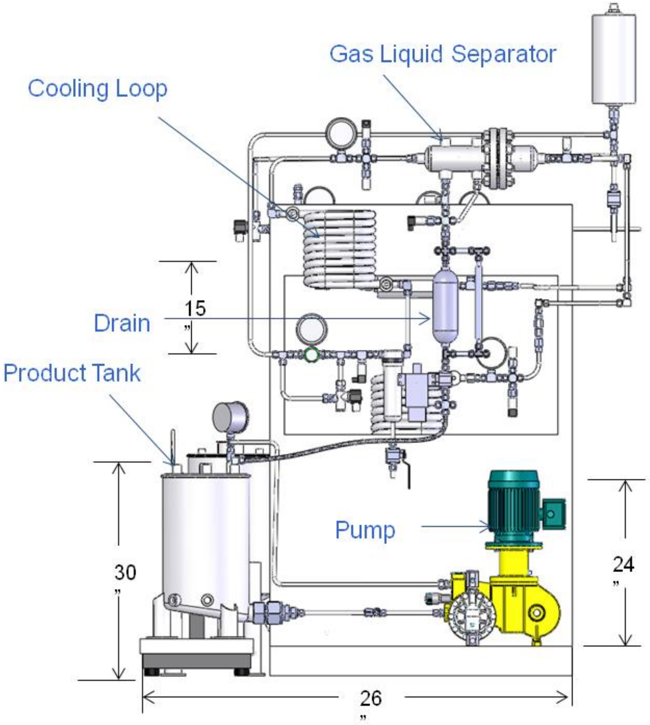
- Beginning of Phase 2 (03/31/2011):
  - Transitioned from solid AB to AB in a fluid form (liquid or slurry).
  - NH_3 sorbent with 5 wt% dynamic sorption capacity.

Flexible screw auger

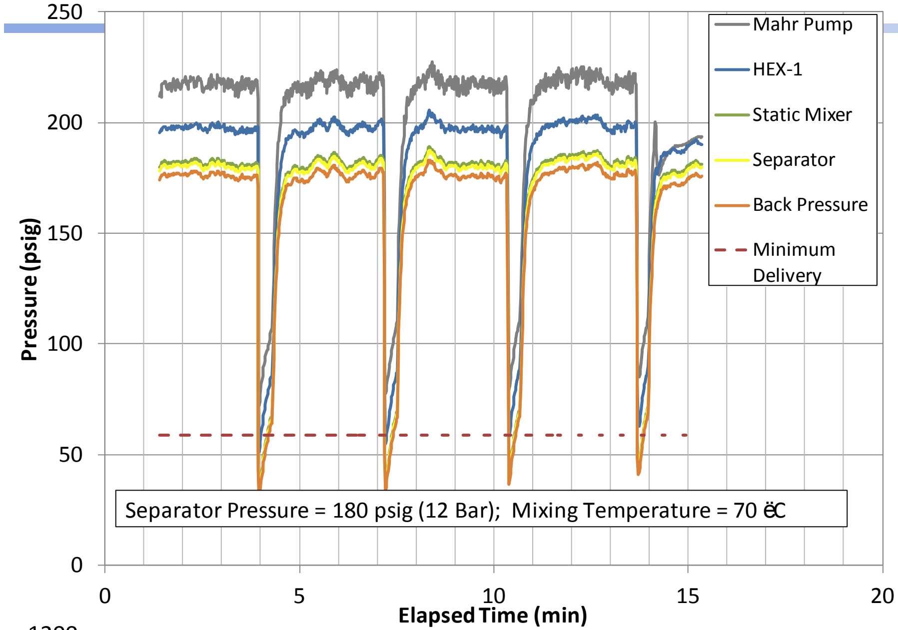
- Last Tech Team Review (02/15/2012):
  - Designed a gas-liquid separator test facility.
  - Selected custom designed static gas-liquid separator (GLS).



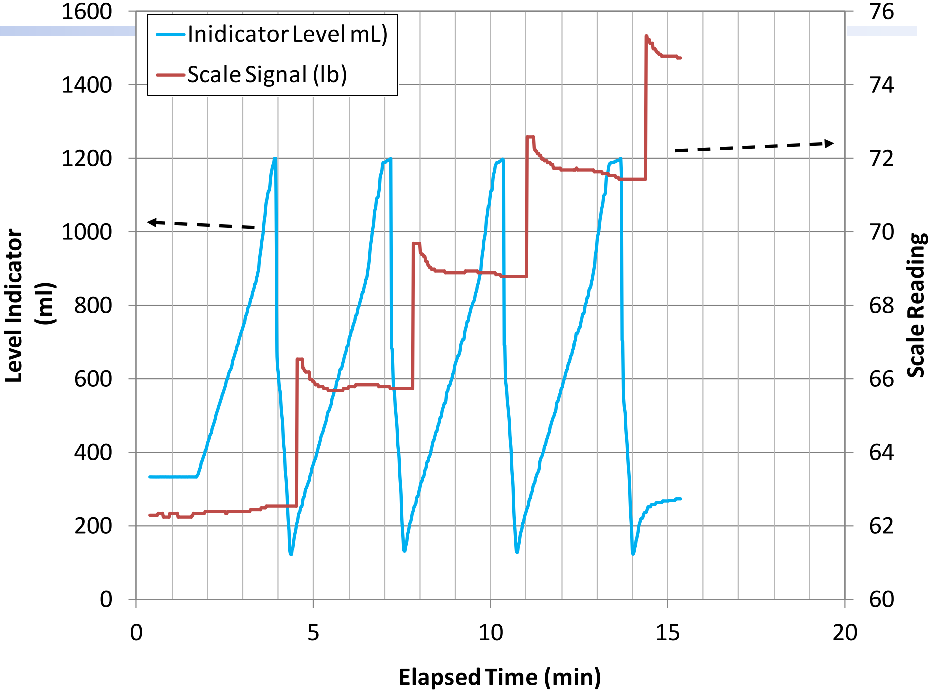
  - Reported high dynamic sorption capacity NH_3 sorbent (11 wt%).

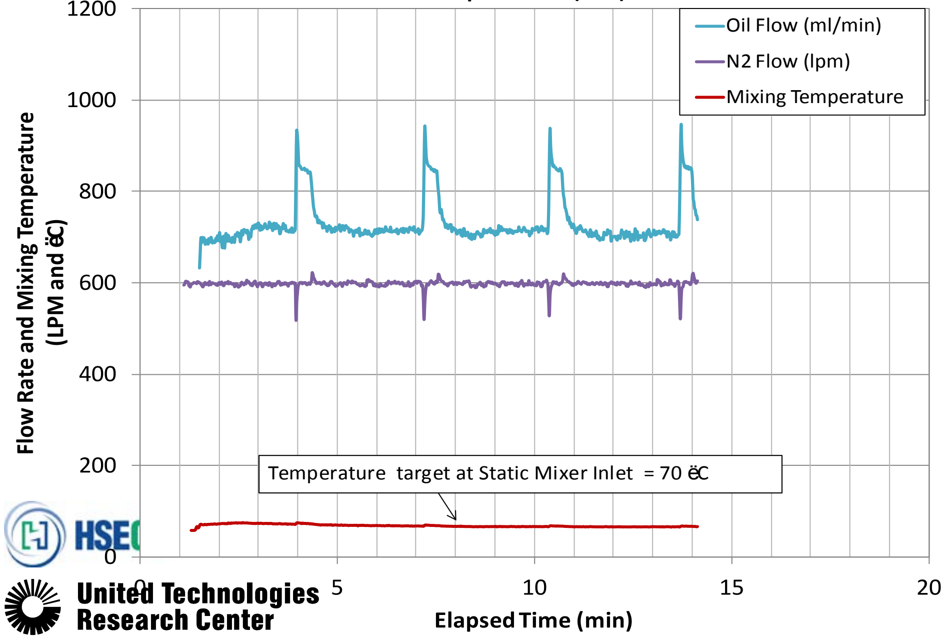


GLS system operating characteristics



Separator Pressure = 180 psig (12 Bar); Mixing Temperature = 70 ëC





Temperature target at Static Mixer Inlet = 70 ëC

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