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

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HSECoE

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Annual Merit Review
Washington, DC
June 18, 2014

Project ID: ST006

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Overview

- **Timeline**
  - Project Start Date: 2/1/09
  - Project End Date: 6/30/15
- **Budget**
  - Total Project Value: $5.46
  - Cost Share: $1.15 M
  - DOE Share: $4.31M
  - Total Funding Spent*: $4.25M
- **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, Hexagon Lincoln, OSU Oregon State University, HRI UQTR, GM, Ford, BASF The Chemical Company, JPL, California Institute of Technology, NREL National Renewable Energy Laboratory, HSECoE, IEA HIA Task 32

* As of 3/31/14

** DOE EERE FCTO 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

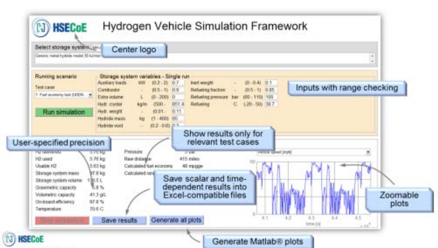
Performance Measure	Units	2017	Ultimate
System Gravimetric Capacity	g H_2 /kg system	55	75
System Volumetric Capacity	g H_2 /L system	40	70
System fill time (for 5 kg H_2)	minutes	3.3	2.5
Fuel Purity	% H_2	SAE J2719 guideline (99.97% dry basis)	

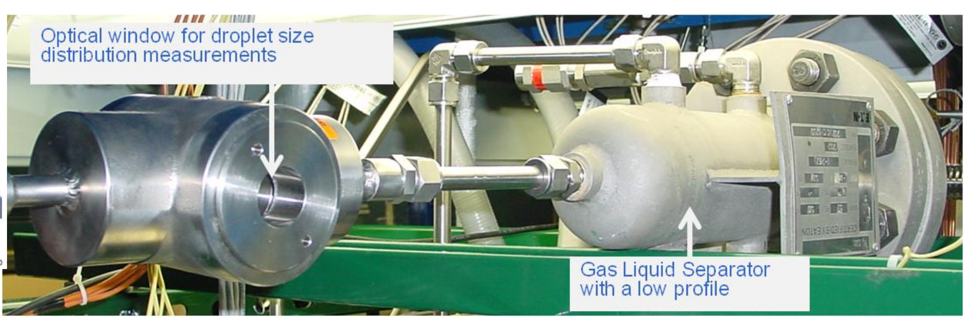
- Major project impact:
  - Gas/Liquid separator (GLS) for liquid chemical hydrogen storage system
  - H_2 quality (NH_3 and particulate filter)
  - Improved chemical hydrogen storage system's gravimetric capacity from 31 to 41 g H_2/kg system and the system's volumetric capacity from 36 to 40 g H_2/L system (=2017 target) by reducing weight and volume of BOP components.
  - Integrated Power Plant Storage System Modeling (IPPSSM):
    - Compared H_2 storage systems on a common basis
    - Supported storage system model integration
    - Developed GUI for models on the web (at: www.hsecoe.org)

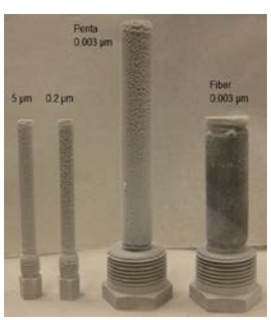
Phase 3 S*M*A*R*T Milestones and Status

S*M*A*R*T Milestone	Status
Report on ability to develop a gas/liquid separator with a specific Souders-Brown velocity of >0.013 (m/s)/kg and >0.029 (m/s)/L.	✓ Mass 5.8 kg, Volume 2.7 L, 3” ID 16 bar, 0.72 lpm oil, 300 slpm N_2 Souder-Brown velocity for N_2: 0.015 (m/s)/kg (meets target) 0.032 (m/s)/L (meets target)
Report on ability to develop an ammonia filter cartridge with <27 kg/kgNH_3 and <22 Liter/kg NH_3 that enables a purified gas with <0.1 ppm NH_3 (SAE J2719 guideline).	✓ Including housing: 27.6 kg/kg-NH_3 (meets target) 22.1 L/kg-NH_3 (meets target)
Report on the ability to filter particulates in gas from a cryo-adsorbent bed to less than 1000 µg/m^3 and 10µm diameter (SAE J2719 guideline).	✓ 0.01 µg/m^3 (i.e. <<1000 µg/m^3) (meets target) Some >10µm particles (0.01 µg/m^3): Stringent system cleanliness procedures
Update the cryo-adsorbent system model with Phase 3 performance data, integrate into the framework; document and release models to the public.	On Track: Difficulty to run adsorption based H_2 storage system to completion (5.6 kg H_2 delivered)

Mass and volume of UTRC’s BOP components reduced from 28% to <5% by mass and from 12% to <3% by volume of total system







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Approach

- Gas liquid separator (GLS):
  - Demonstrate S*M*A*R*T milestones with surrogate materials
  - Develop GLS model
  - Validate GLS model experimentally
- H_2 quality:
  - Qualitative and quantitative analysis of impurities resulting from fluid form of chemical hydrogen storage material (AB in silicone oil AR20)
  - Test particulate filters for MOF-5
  - Extended analytic capability to measure particulate size from 0.5 μm to 32 μm
- Simulink Framework:
  - Develop graphical user interface (GUI) architecture and perform beta-tests
  - Provide Simulink® Framework with physical storage and metal hydride model for web-version
  - Support integration of other H_2 storage models in framework
  - Apply framework to assess GLS operating requirements

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

Collaborations

	Cryo-adsorption: • Particulate mitigation • Sharing best practices
	Chemical hydrogen storage: • Process development • BOP components • Testing of GLS with surrogate material
	H_2 storage system models: • 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, SNL and ANL

MODELS ON THE WEB

PLEASE VISIT: WWW.HSECOE.ORG

Framework with Graphical User Interface (GUI)

Preparation for publishing the Framework/GUI on the HSECoE website

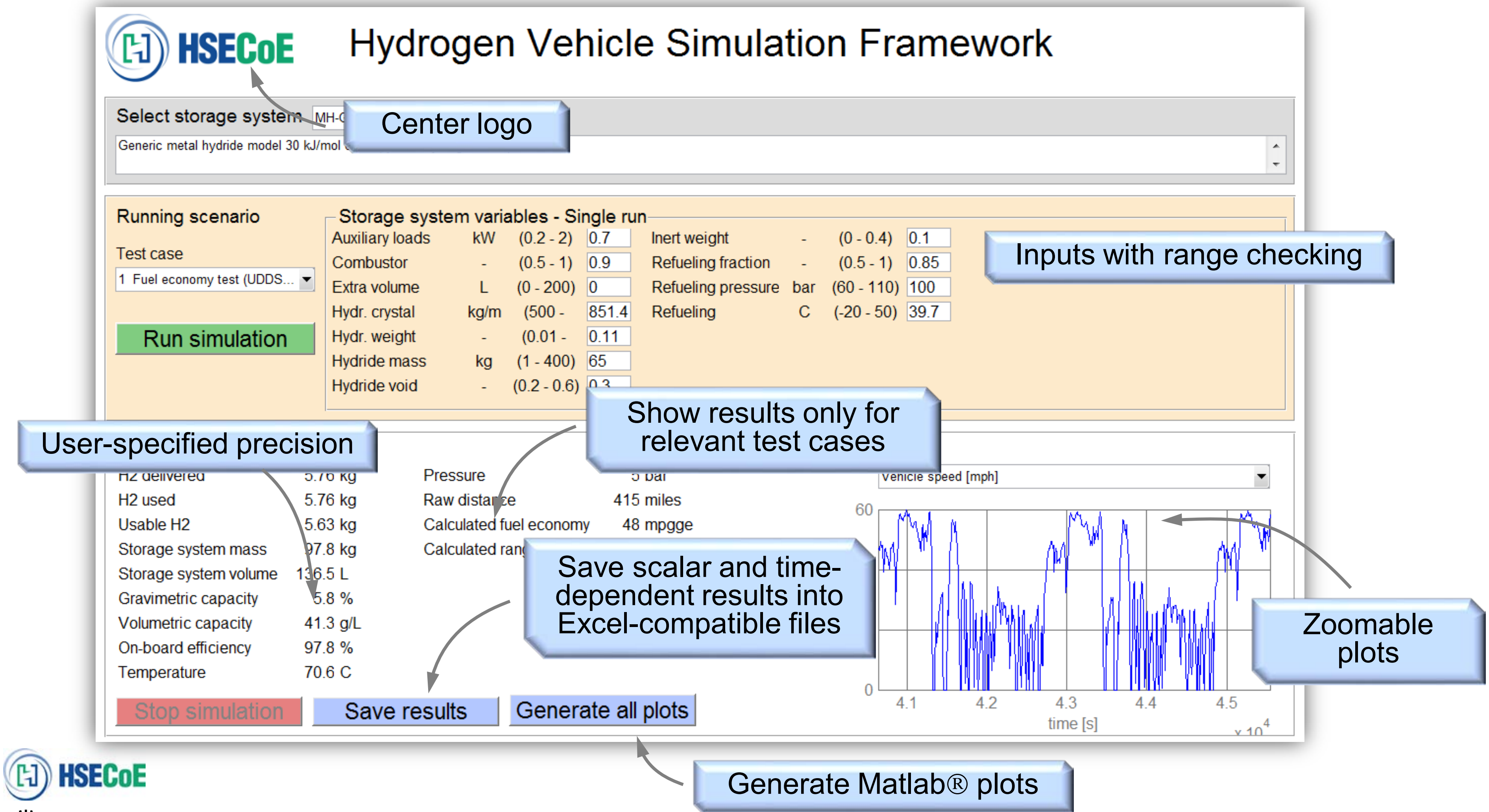
- Close UTRC/NREL interaction to improve simulation speed > 20x.
- Improved documentation.
- Four systems published on the HSECoE website: **http://www.hsecoe.org/**
  - Test system: for isolated running of fuel cell and vehicle.
  - Compressed: 350 bar, 700 bar.
  - Ideal metal hydride system.

Updated GUI based on feedback from Tech. Team and beta testers.

- Improved Excel-compatible output.
- Show results only when relevant for the test case.
  E.g., EPA fuel economy is only meaningful in Test Case 1.

Interface improvements based on feedback

- Metal hydride storage system model example in Simulink® framework

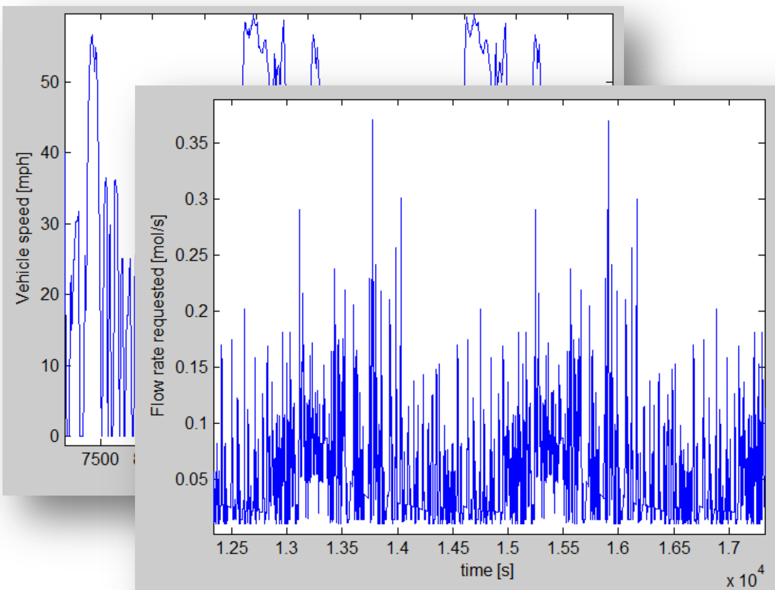


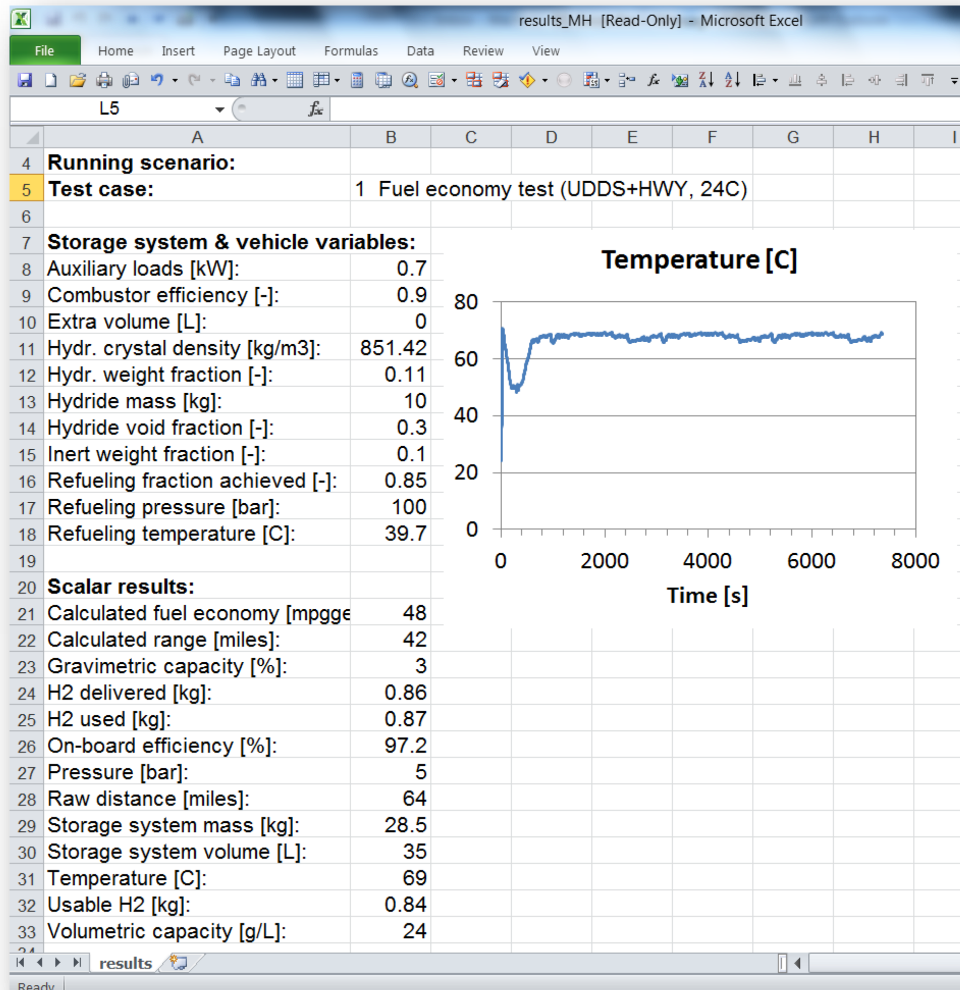
Interface improvements based on feedback

- Improved connection to external tools

Generate Matlab® plots
For further editing

Save results into
Excel-compatible files



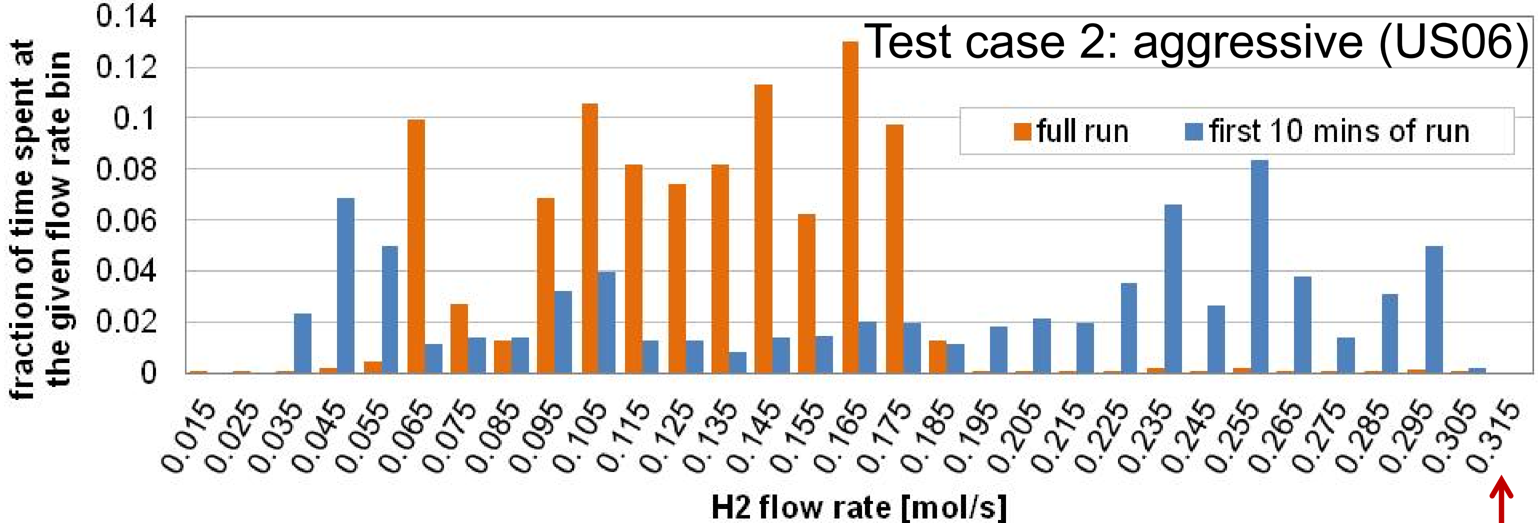


Running scenario:	
Test case:	1 Fuel economy test (UDDS+HWY, 24C)
Storage system & vehicle variables:	
Auxiliary loads [kW]:	0.7
Combustor efficiency [-]:	0.9
Extra volume [L]:	0
Hydr. crystal density [kg/m3]:	851.42
Hydr. weight fraction [-]:	0.11
Hydride mass [kg]:	10
Hydride void fraction [-]:	0.3
Inert weight fraction [-]:	0.1
Refueling fraction achieved [-]:	0.85
Refueling pressure [bar]:	100
Refueling temperature [C]:	39.7
Scalar results:	
Calculated fuel economy [mpgge	48
Calculated range [miles]:	42
Gravimetric capacity [%]:	3
H2 delivered [kg]:	0.86
H2 used [kg]:	0.87
On-board efficiency [%]:	97.2
Pressure [bar]:	5
Raw distance [miles]:	64
Storage system mass [kg]:	28.5
Storage system volume [L]:	35
Temperature [C]:	69
Usable H2 [kg]:	0.84
Volumetric capacity [g/L]:	24

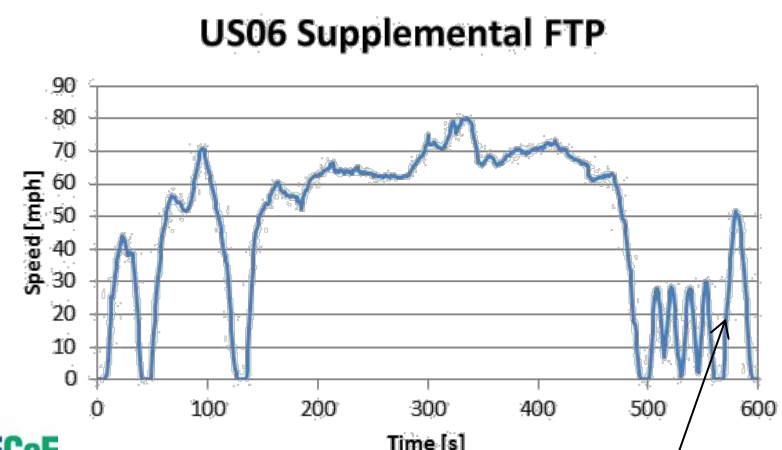
Guidance for GLS Operating Conditions

Temperature: ~200-250°C
Pressure: ~25 bar

Relative frequency
(first bin not included - reactor initially inactive)



31.5 kW_e (@0.02 g/s/kW_e)
Occasionally: 80 kWe



From 0 to 50 mph
in 10 seconds

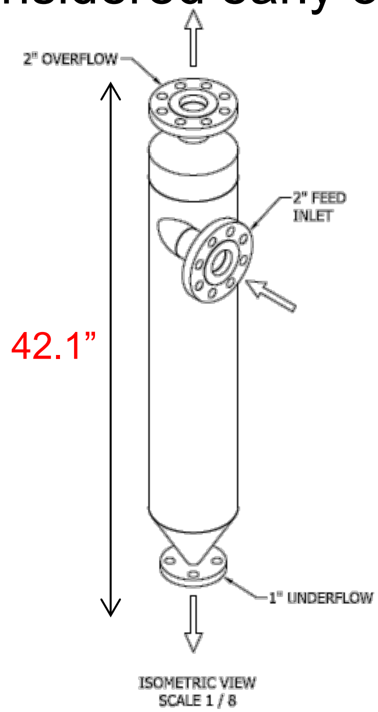
- Designed GLS capable of 0.8 mol/s (~80 kWe).
- GLS also serves as buffer volume.

GAS/LIQUID SEPARATOR MODEL & VALIDATION

Selection of GLS-type

Status at Beginning Phase 2

- Vertical design was considered early on

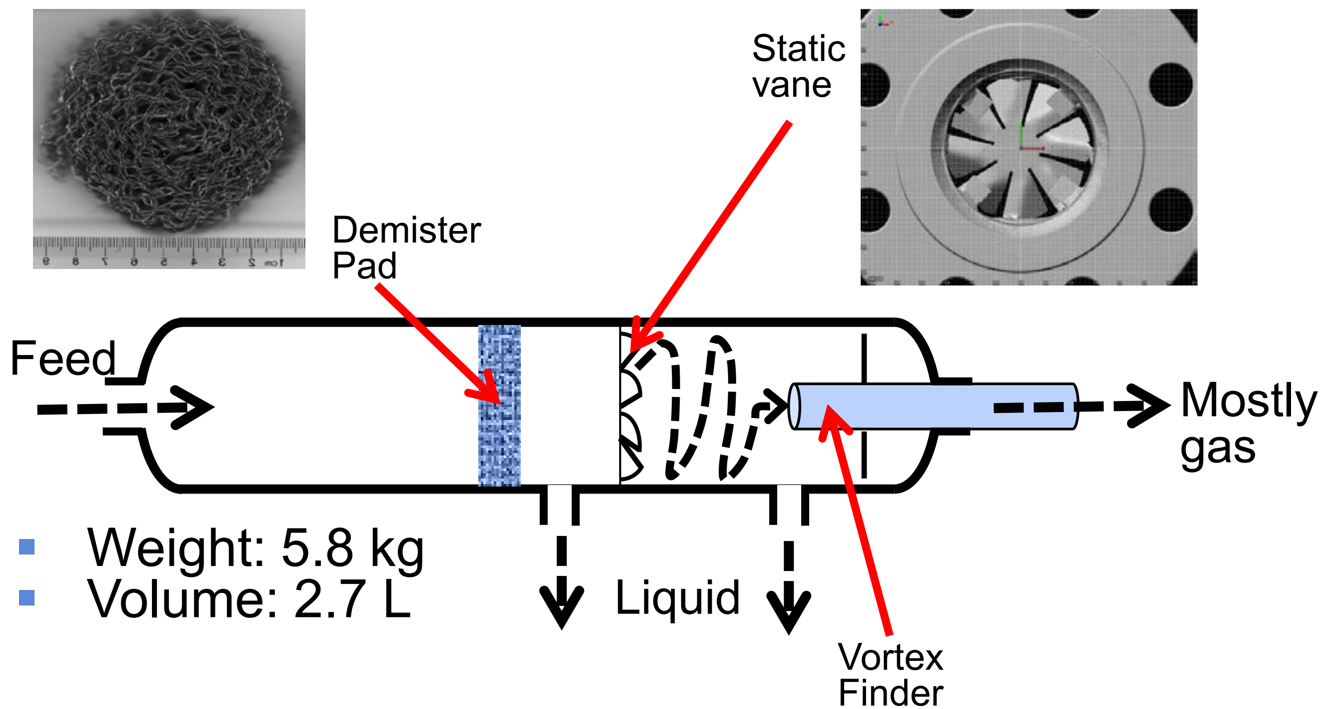


- Weight: 51 kg
- Volume: 19 L

Current Status

Relentless system weight and volume reduction

- Horizontal for low profile
- No rotating part for reliability/cost/on-board efficiency



- Weight: 5.8 kg
- Volume: 2.7 L

System aspect	Beginning Phase 2	Current	2017 Target
g H_2/kg system	31	41	55
g H_2/L system	36	40	40

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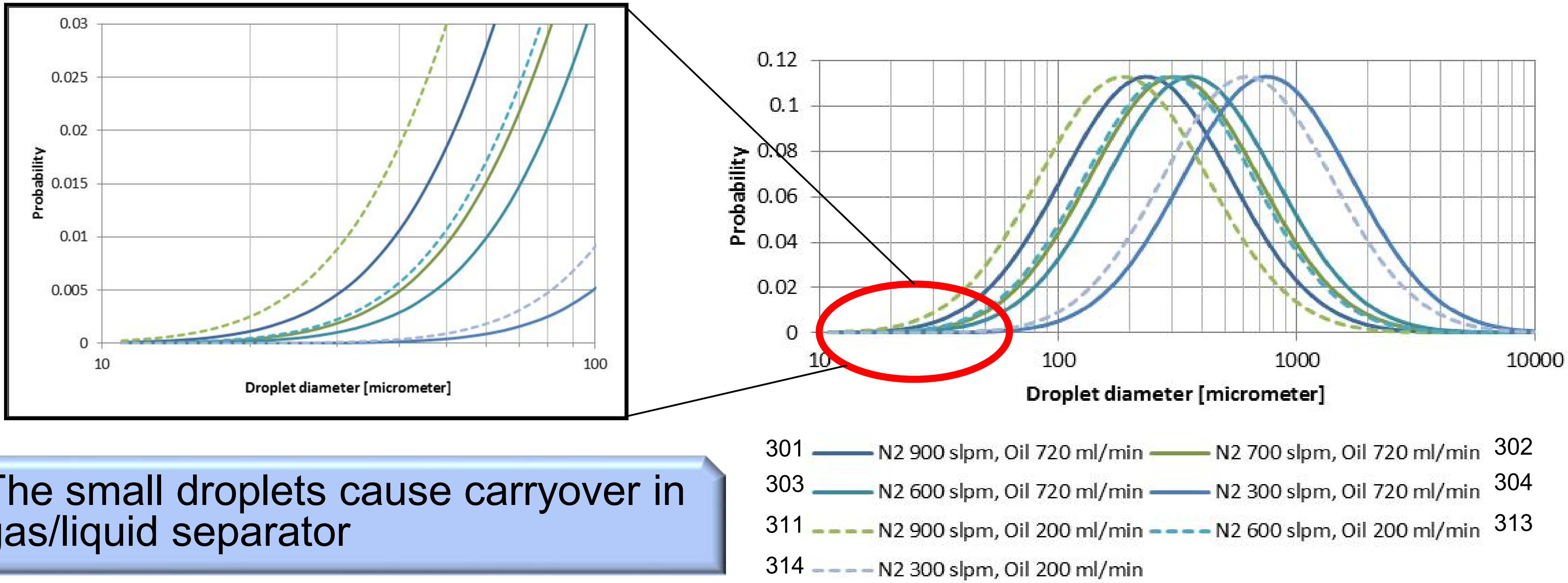
Inlet Boundary Condition for CFD Model

- Used drop size correlation* for two-phase annular flow in order to estimate droplet size distribution at inlet of GLS

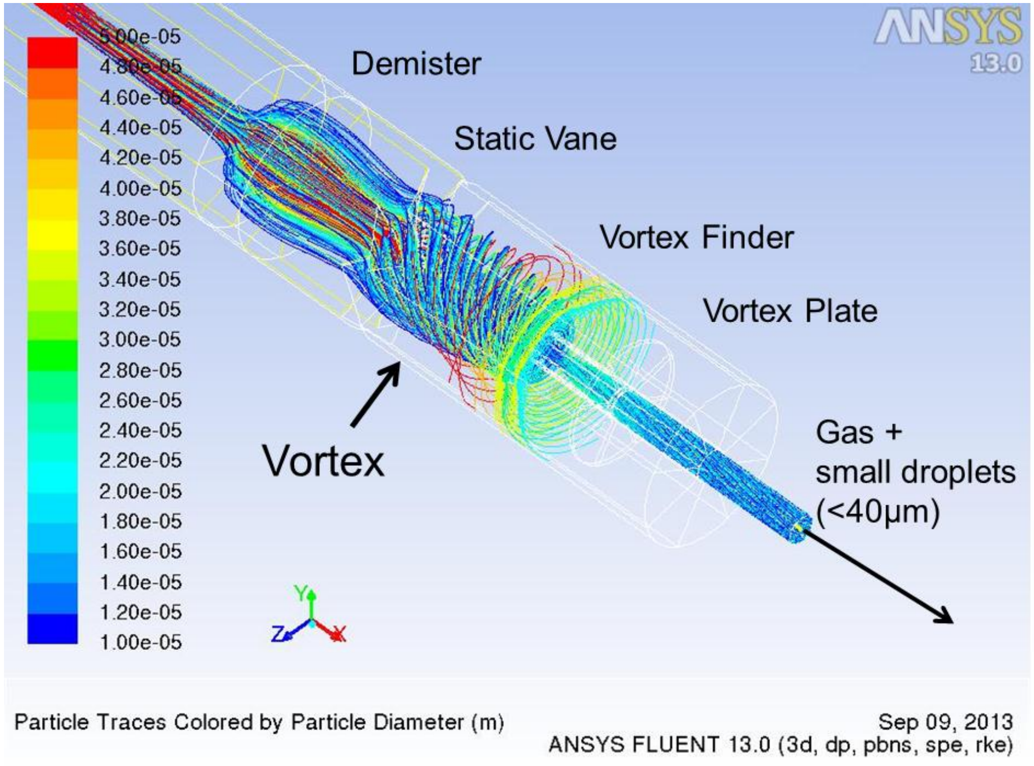


The small droplets cause carryover in gas/liquid separator

*Ref.: B.J. Azzopardi, Drops in Annular Two-Phase Flow, Int. J. Multiphase Flow, Vol. 23, 1997, Suppl., pp. 1-53

Droplet Traces

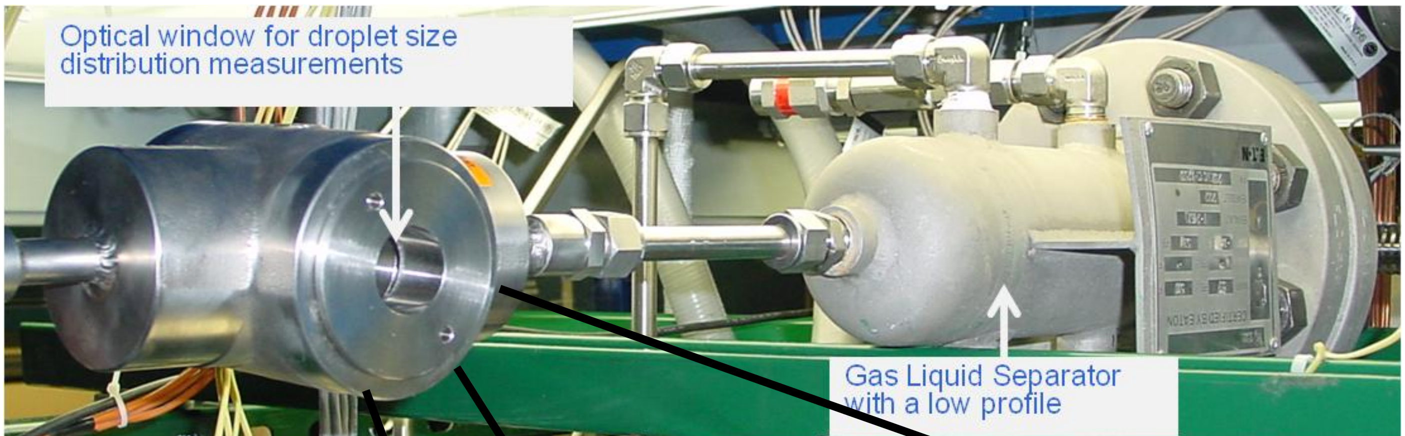
- Operating conditions:
  - 70°C, 12 bar, AR20 Silicone oil: 0.2 slpm, N_2: 900 slpm
- Steady state
- All droplets hitting the wall inside the GLS are considered to form a film that can be drained
- Model can be used for sizing the GLS



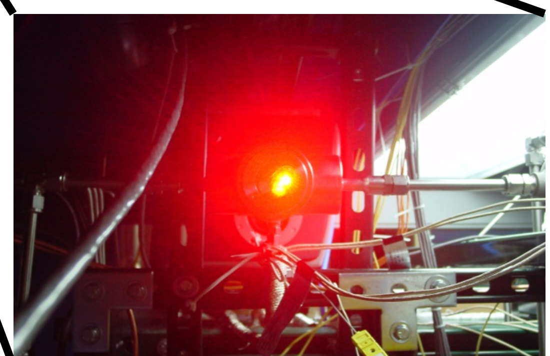
Small droplets (<50 μm) follow the streamlines of the gas

Experimental

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



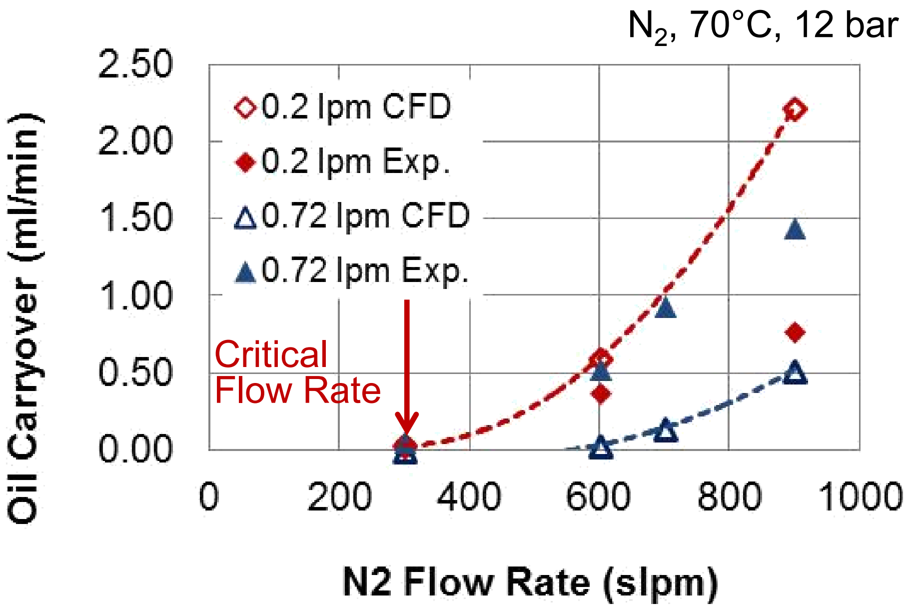
Keeping the optical window clean is a real challenge



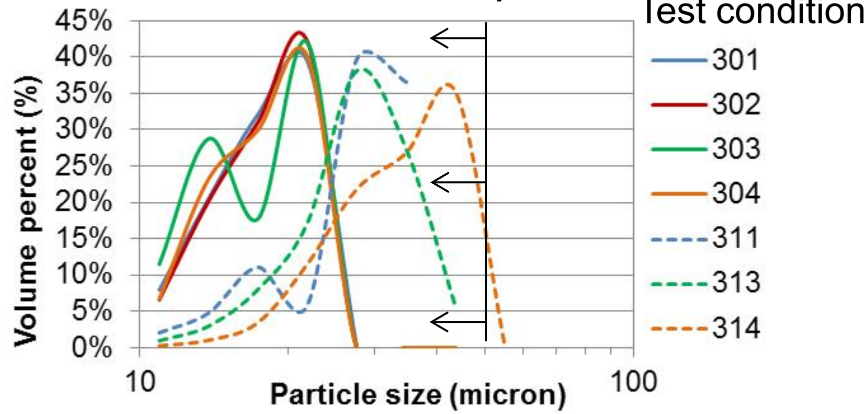
Laser scattering with Malvern Mastersizer

Model validation

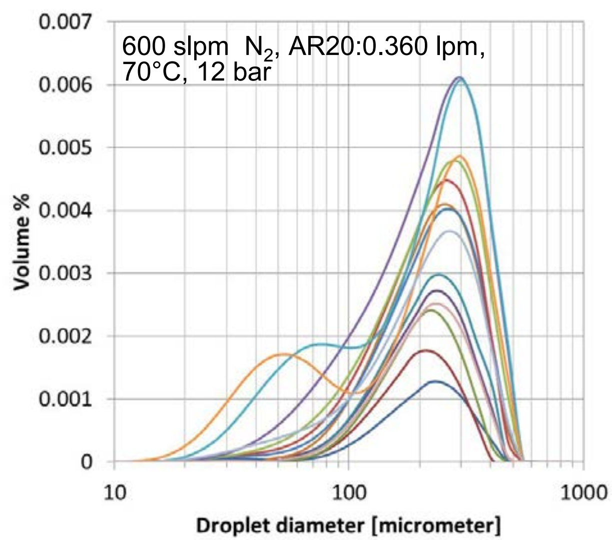
- Comparison with CFD Model



- Calculated outlet droplet size <50μm



- Measured outlet droplet size



- Good model estimate of N_2 critical flow rate
- H_2 critical flow rate is estimated to be a factor 3.75 higher than the N_2 critical flow rate
- Experimental droplet size appears larger than predicted by CFD model due to filming in the vortex finder

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GLS Development

- Souders-Brown equation to convert from N_2 to H_2:

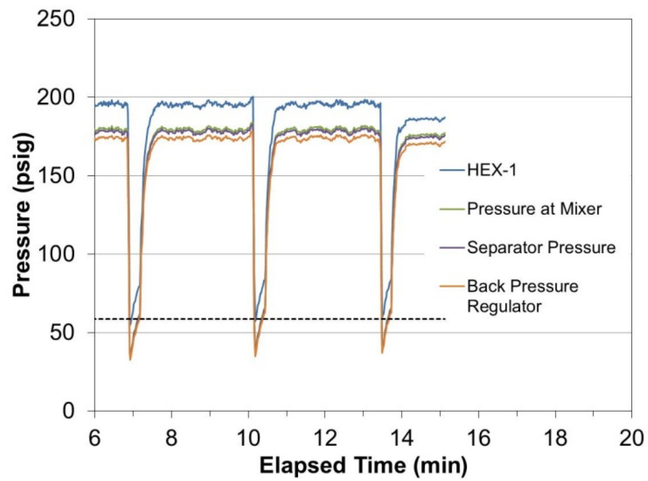
$$K_{value} = u_g \sqrt{\frac{\rho_g}{\rho_l - \rho_g}}$$

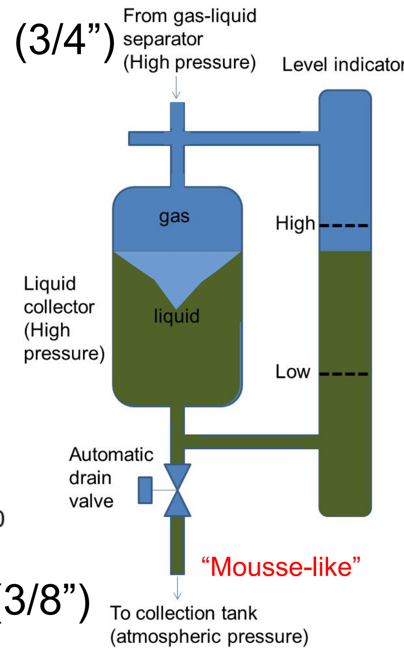
$$u_{g,H2} \sim 3.75 * u_{g,N2}$$

- Critical N_2 gas velocity (300 slpm, 16 bar, 70°C) scaled to GLS weight (5.8 kg) and volume (2.7 L):
  - 0.015 (m/s)/kg
  - 0.032 (m/s)/L
- The current GLS is sufficient to support 80 kW_e peak power in aggressive drive cycle

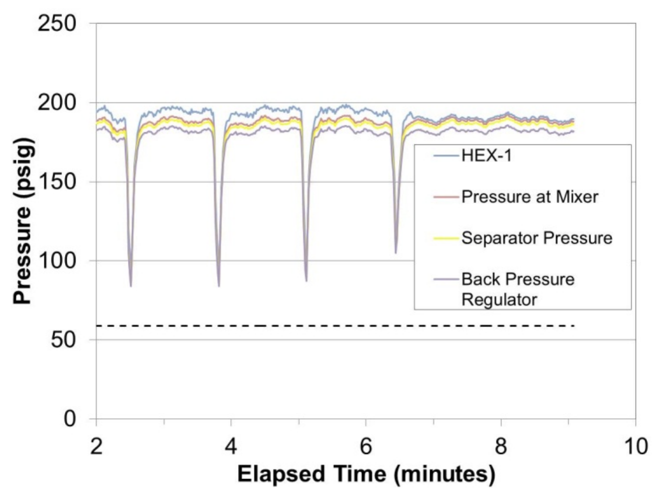
S*M*A*R*T milestone achieved

- Operational Issues
- Drain valve coefficient Cv=13.6 (3/4")





- Drain valve coefficient Cv=3.8 (3/8")



Drain system improved in order to maintain system pressure

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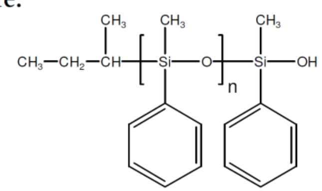
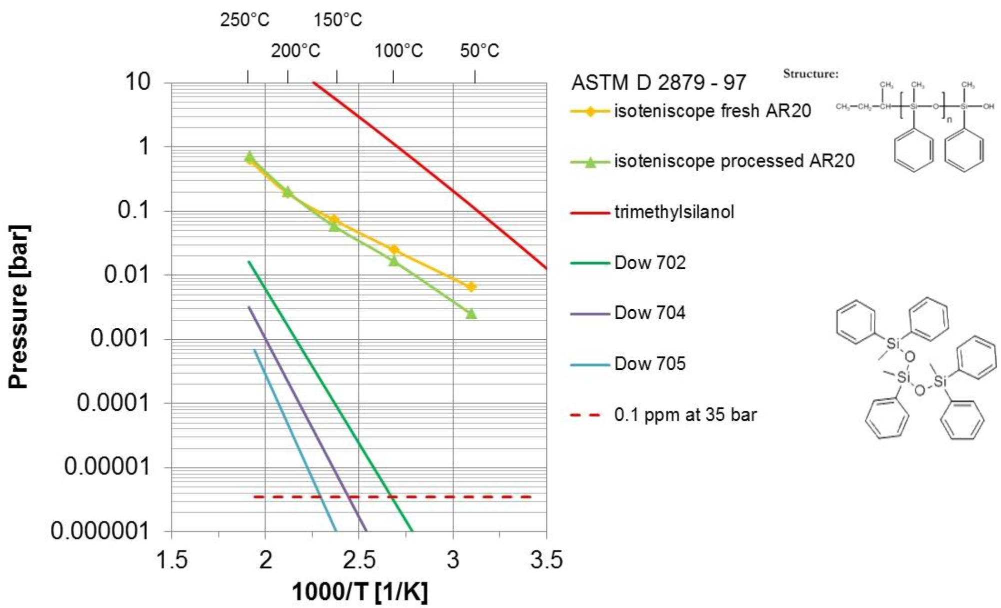
H_2 QUALITY

H_2 Quality Affected By Slurry Agent

- Silicone Oil AR20 has significant vapor pressure

Structure:





- Silicone Oil AR20 contaminates H_2 with numerous components

Component	MW [g/mol]	ppm by weight	ppm by volume (25°C, 1atm)
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

- UTRC identified fluids for forming AlH_3 or AB slurries that have a low vapor pressure in order to minimize impact on H_2 quality

High vapor pressure of AR20 forced GLS temperature to be reduced to 70°C.

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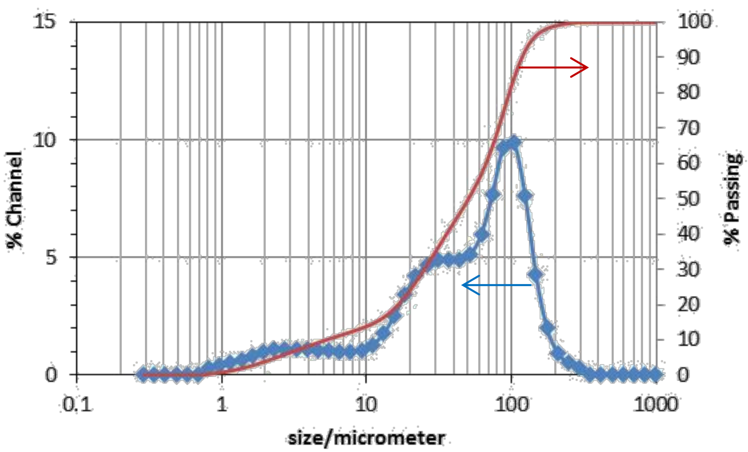
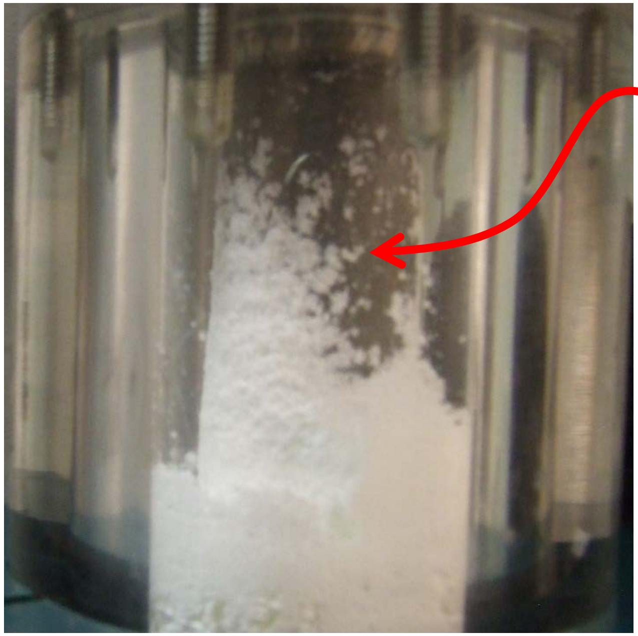
Particulate Filter Selection

- Two mechanisms:
  - 1st : Particles penetrate deeply into the filter media (depth filtration)
  - 2nd : Particles accumulate as a cake on the filter surface

> Surface filters are a more practical proposition than depth filters for long-term operation of industrial processes with high dust concentrations

MOF-5 particle size distribution:



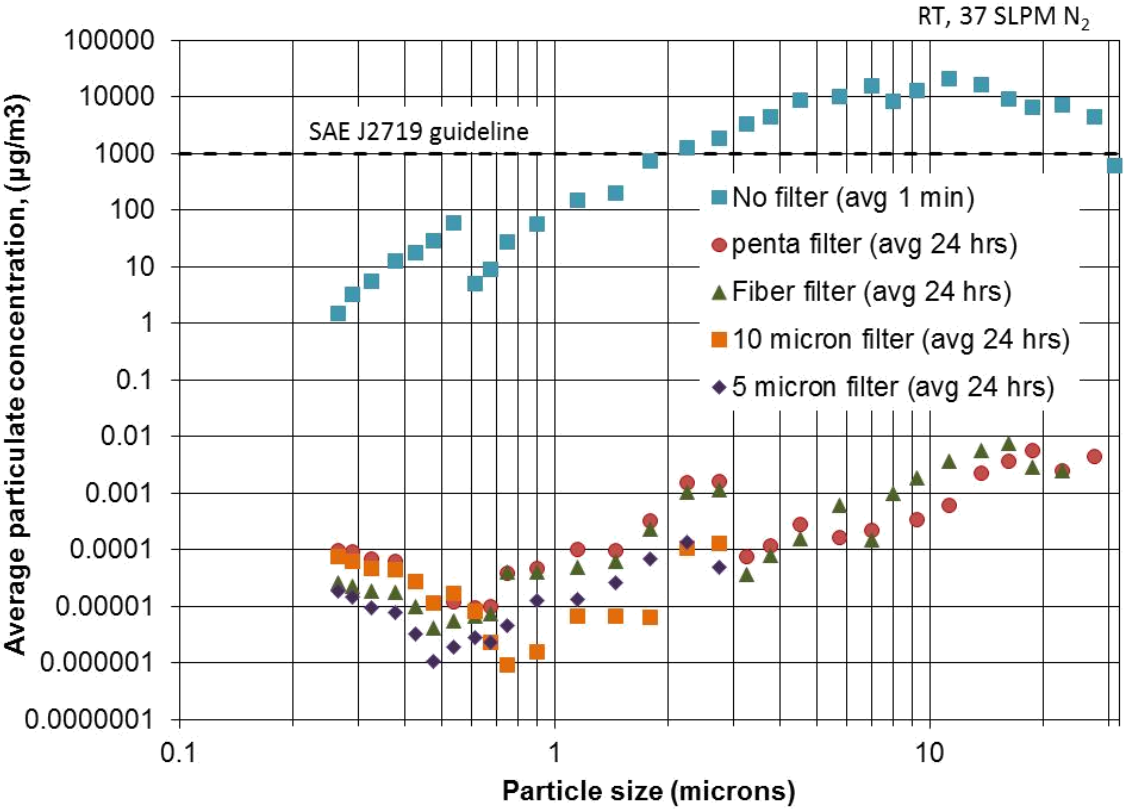


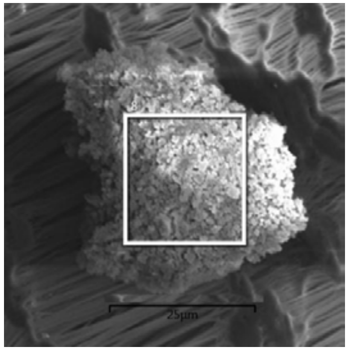
MOF-5 flakes

Conditions:
~20 slpm N_2
Atmospheric pressure
Room temperature
Fiber-filter

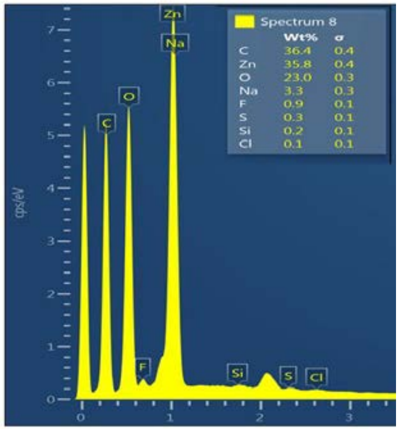
Particulate Concentration (250 nm – 32 μm)

- Analyzer: Grimm Model 1.109 with span from 250 nm to 32 μm in 31 bin sizes





SEM picture of MOF-5 agglomerate



EDX analysis of MOF-5 particulate

UTRC expanded particulate size range of its analytical capability; All 4 studied filters enabled meeting the SAE guideline. Right sizing of filter area is important.

FY14 and FY15 Plan

Task	Description	FY14 1Q	FY14 2Q	FY14 3Q	FY14 4Q	FY15 1Q	FY15 2Q	FY15 3Q
Project Management	End of Phase 3							
	F2F-meetings; Tech Team Review; Annual Merit Review							
	Quarterly Financial and Technical Reports							
	Develop final reports with UTRC's contribution to HSECoE							
Integrated Power Plant Storage System Modeling (IPPSSM)	Lead IPPSSM Techical Area (TA)							
	Release Simulink framework with basic models for external users							
	Add chemical hydrogen storage system model to released framework							
	Establish cryo-adsorbent system model functionality in framework							
	Cryo-adsorbent system fully functional in framework							
	Add cryo-adsorbent system model to released framework							
	Update cryo-adsorbent system model to reflect sub-scale results							

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:

- Developed graphical user interface (GUI) and performed beta tests.
- Supported integration of H_2 storage models into framework for public release.
- Demonstrated Gas/Liquid Separator (GLS) S*M*A*R*T milestone with surrogate material.
- Developed and validated model of GLS system.
- Analyzed impurities resulting from the silicone oil AR20.
- Identified alternate fluids with low vapor pressure for slurry development.
- Demonstrated H_2 quality requirements with MOF-5 particulate filters.
- Quantified drop in filter permeability due to filter cake formation.

Future Work:

- Finalize Simulink framework development
- Develop final report

Answers to questions by reviewers

- The Gas/Liquid Separator (GLS) development was brought to an orderly completion soon after the DOE decided to move forward with sub-scale prototyping of two cryo-adsorbent systems (Flow-through cooling and MATI). UTRC was informed by DOE to complete the work with the pure silicone oil AR-20, without increasing complexity by turning the silicone oil into a slurry with a polyimide powder that was identified by PNNL (simulating a spent AB slurry).
- The GLS for the chemical hydrogen storage system was scaled-down substantially in order to achieve weight and volume targets (S*M*A*R*T milestones) and did not yet exist in this form prior to Phase 2 of the HSECoE project. This created uncertainty in the GLS performance which was addressed through CFD modeling of the fluid flow and experimental tests.
- During Phase 2, it was made very clear that LANL and PNNL were going to be the only two laboratories where the exothermic thermolysis of AB was going to be tested. UTRC simulated the effluent of the AB thermolysis reactors with a static mixer for silicone oil and nitrogen gas.
- DOE elected to stop all NH_3 sorbent and filter development after the 2013 AMR. UTRC wrote a paper about the sorbent development, which was accepted for publication. UTRC is still developing a paper that documents a model about the dynamic NH_3 sorption by the impurity filter, enabling others to design such filter.
- DOE decided not to pursue a sub-scale prototype development of the chemical hydrogen storage system at the Phase 2 to Phase 3 Go/No-Go meeting, which would have taught more about the system integration aspects.

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 and Jesse Adams, Bob Bowman and Ned Stetson for their outstanding support.

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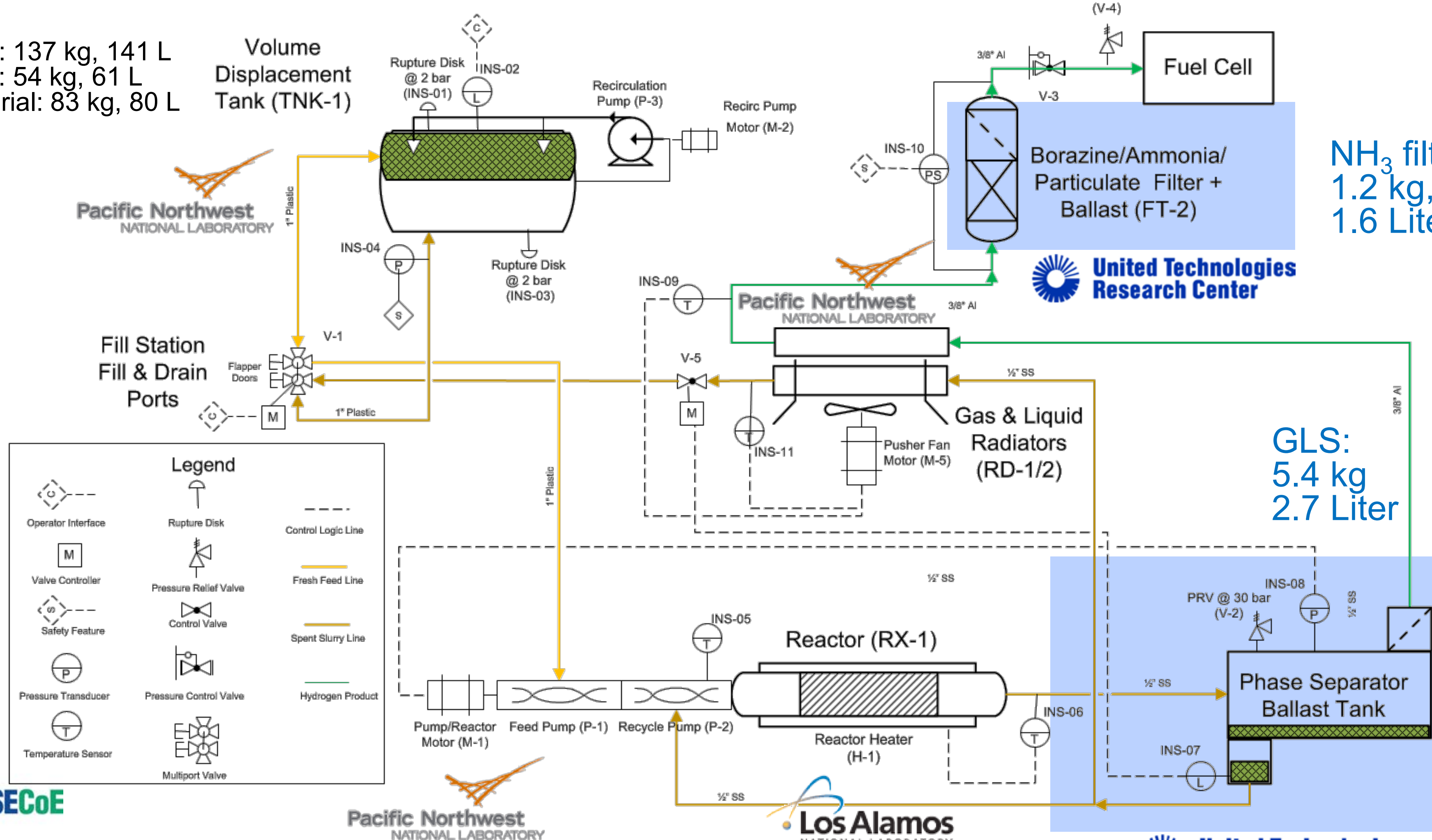
Questions and suggestions?

Technical Back-Up Slides

Demonstrate Engineering Concepts

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

Total: 137 kg, 141 L
BOP: 54 kg, 61 L
Material: 83 kg, 80 L



NH_3 filter:
1.2 kg,
1.6 Liter

GLS:
5.4 kg
2.7 Liter

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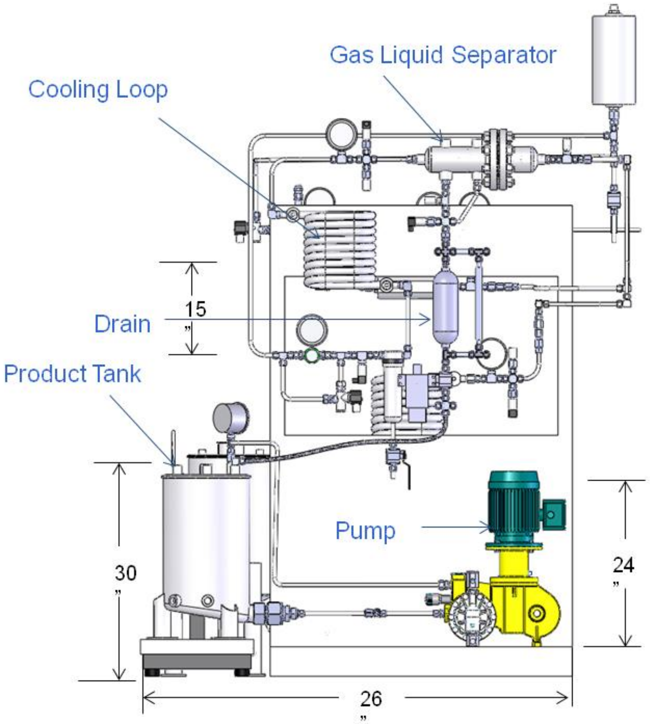
Past Status

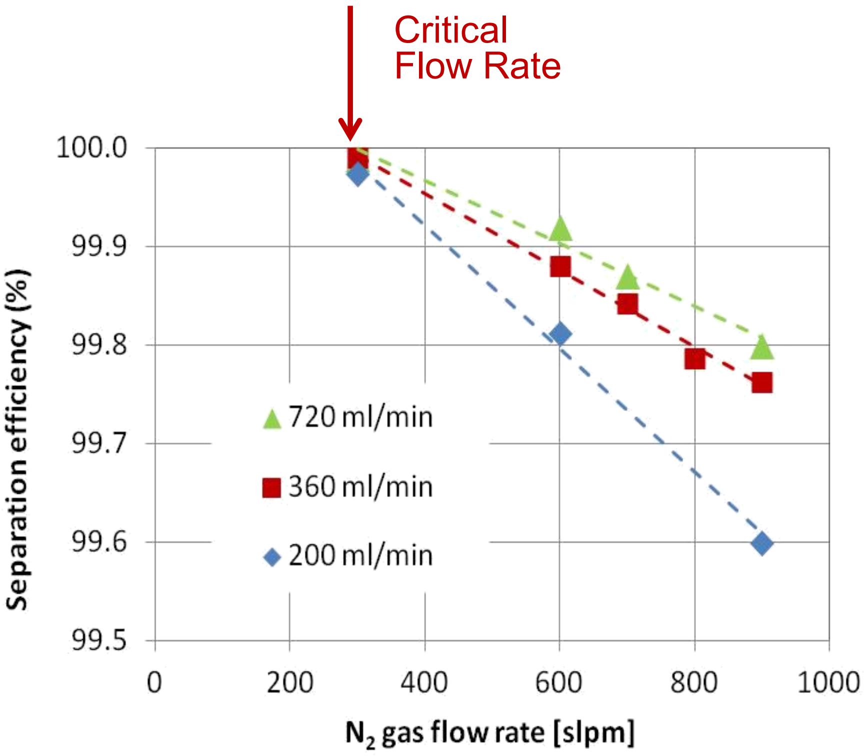
- Last Tech Team Review (03/21/2013):
  - Completed partial design of experiment of GLS with gas flow rate, oil flow rate and temperature as factors
  - Completed development of sorbent materials with high dynamic NH_3 and borazine sorption capacity (NH_3: 11 wt%; borazine: 79 wt%)
  - Demonstrated fuel-cell grade H_2 quality with combined filter



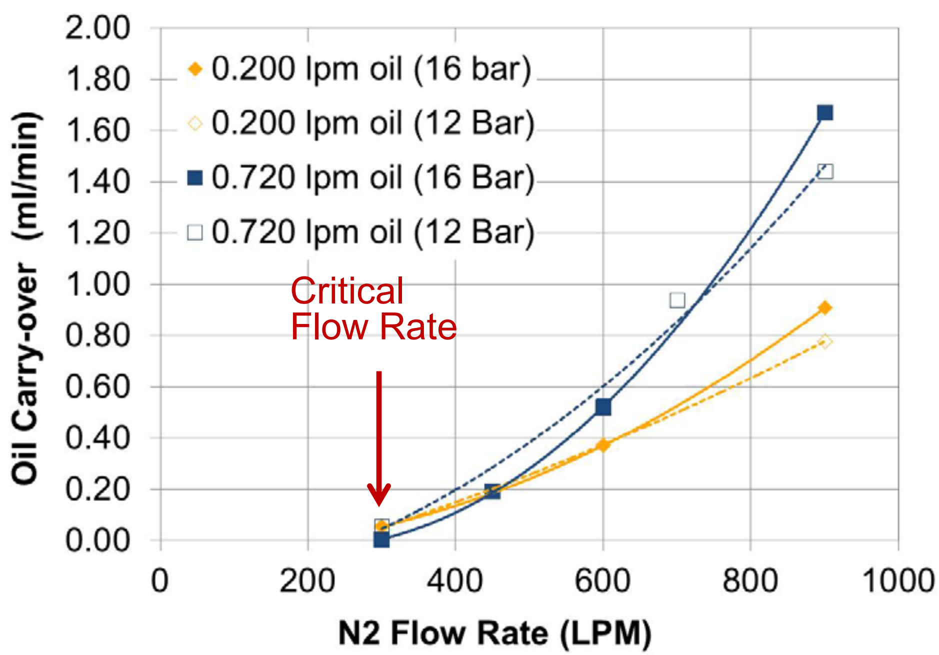
- Beginning of Phase 3 (07/01/2013):
  - Orderly completion of all chemical H_2 storage system engineering:
    - UTRC: Validate GLS model
  - Prepare final report about chemical hydrogen storage system development

GLS Performance

- Separation efficiency(N_2, 70°C, 12 bar)

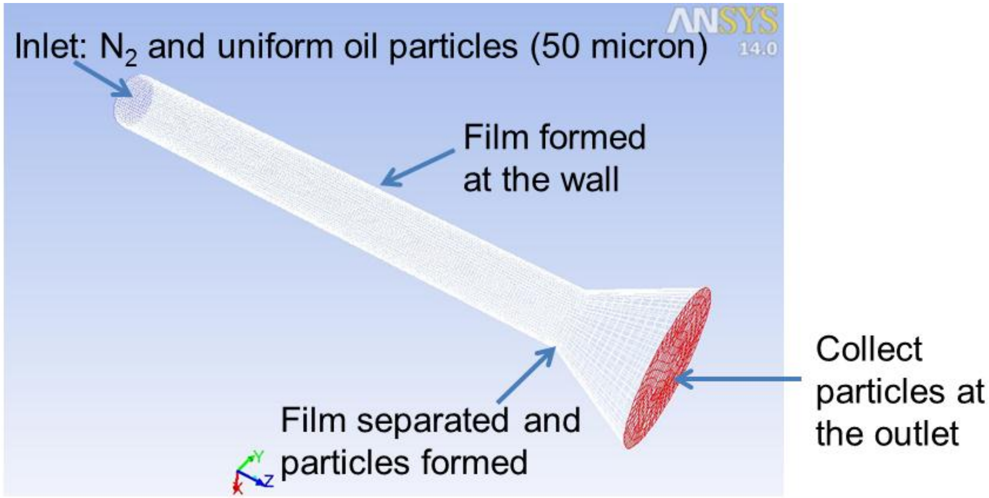


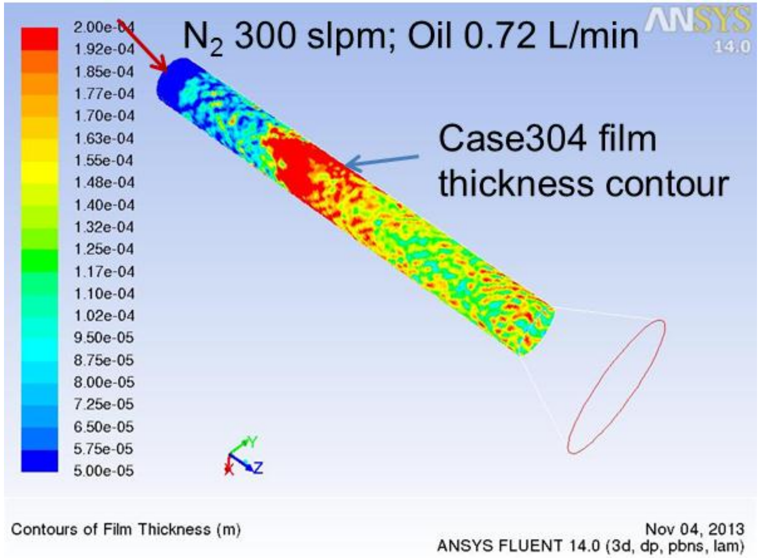
- Carry-over rate (N_2, 70°C) at 12 and 16 bar

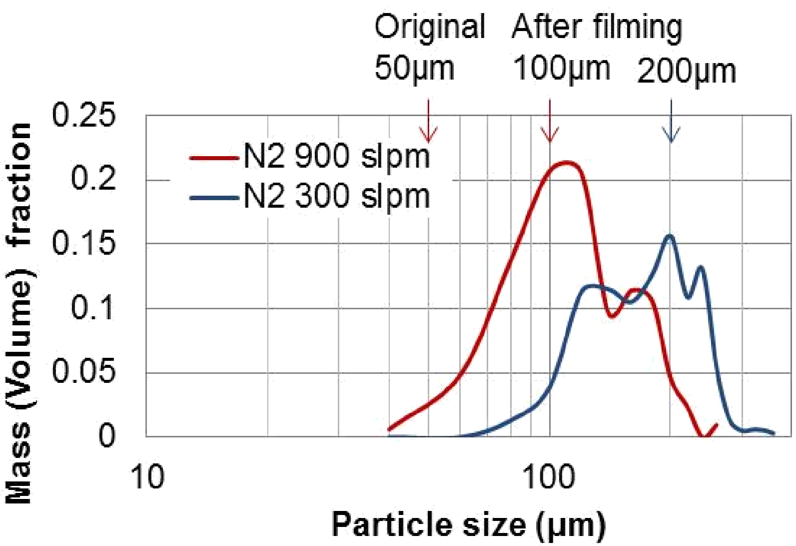


High Performance of Compact GLS

Filming of Silicone Oil Inside Vortex Finder







Filming inside the vortex finder is a mechanism that can generate droplets that are larger than the droplet size at the inlet of the vortex finder.

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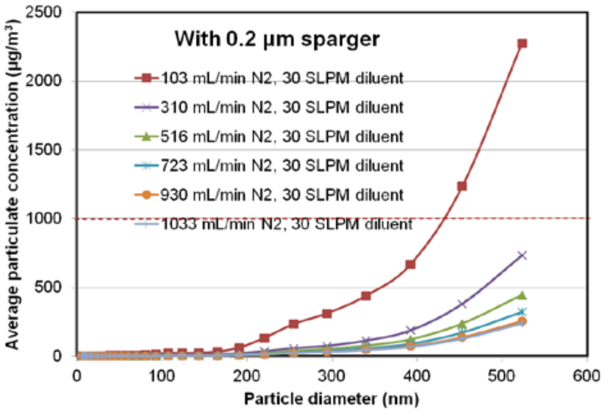
Past Status

- Last Tech Team Review (03/21/2013):
  - Engine Exhaust Particle Size Spectrometer limited particle size to <0.5 μm
  - Porous metal filters tested at relative low flow rate and at room temperature
  - MOF-5 particulate concentration below SAE guideline
- Beginning of Phase 3 (07/01/2013):
  - Assess performance of advanced particulate filters that can be applied to cryo-adsorbent systems with flow through cooling



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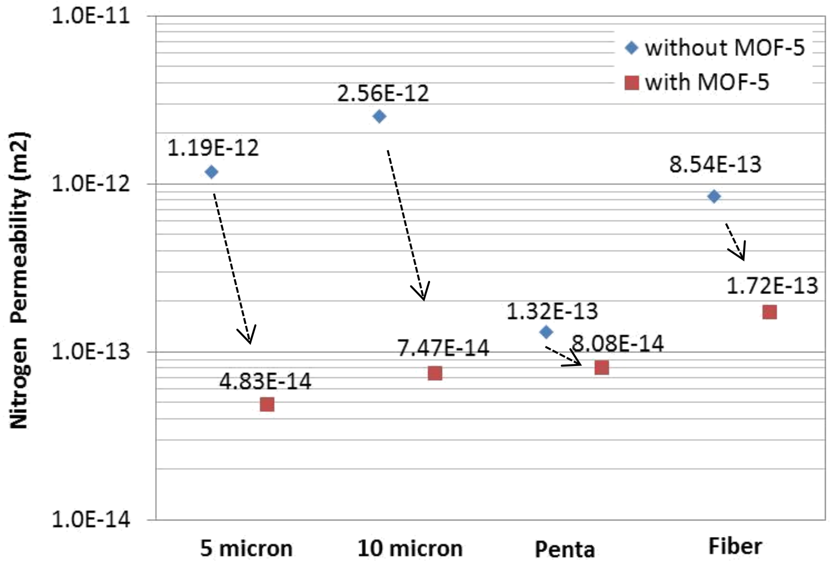
Filter Permeability

- Drop in permeability upon exposure to MOF-5 particulates



Clean Fiber filter

Fiber filter with MOF-5 filter cake

Filter cake breakup by reverse flow during refueling revitalizes the filter.

- Filter description and permeability data

Filter name	Length (m)	Outer diameter (m)	External Area (m^2)	Wall thickness (m)	Inner diameter (m)	Permea-bility without MOF-5 (m^2)	Permea-bility with MOF-5 1st cycle (m^2)	Permea-bility with MOF-5 2nd cycle (m^2)
Penta	0.1207	0.0203	0.0077	0.0018	0.0168	1.32E-13	8.08E-14	8.08E-14
Fiber	0.0635	0.0279	0.0056	0.0051	0.0178	8.54E-13	1.72E-13	1.84E-13
10 micron 6400 series	0.0699	0.0095	0.0021	0.0016	0.0064	2.56E-12	7.47E-14	7.47E-14
5 micron 6400 series	0.0699	0.0095	0.0021	0.0016	0.0064	1.19E-12	4.83E-14	4.83E-14

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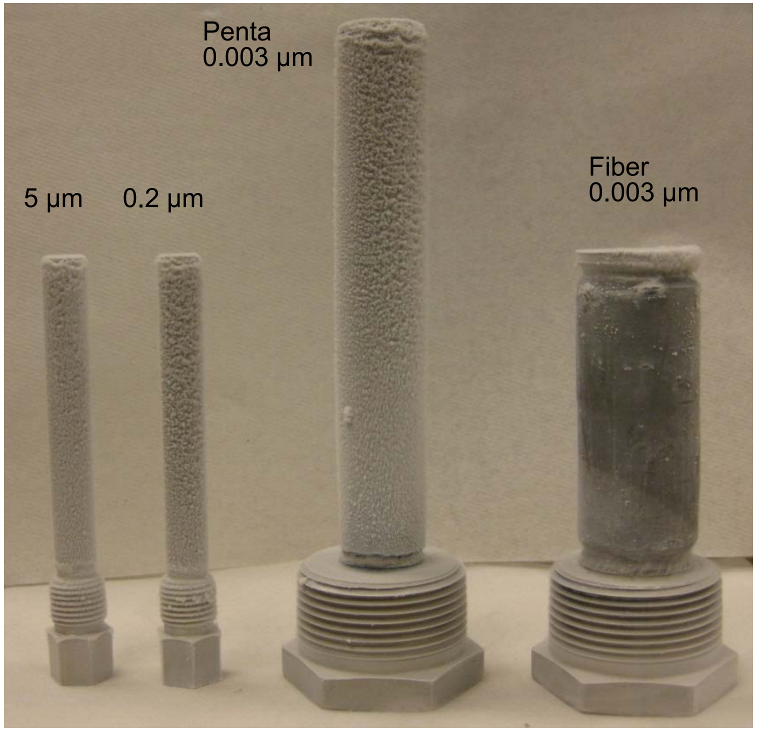
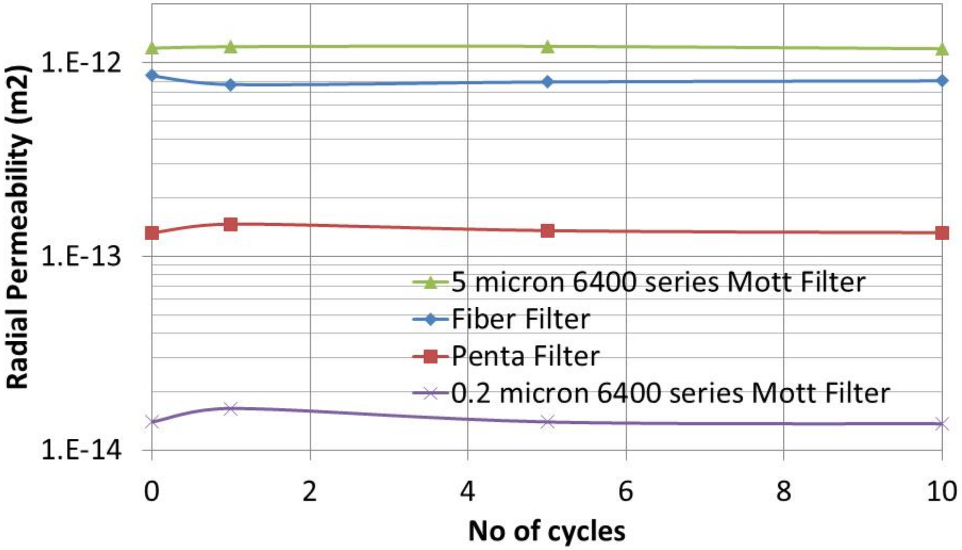
Thermal cycling from RT to 80K

- Porous metal filters



Warming up in air after immersion in liquid N_2

- Darcy flow permeability (N_2) at room temperature



Resistant to thermal cycles between room temperature (RT) and 80K