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


United Technologies Research Center

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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
- Los Alamos National Laboratory
- LINCOLN COMPOSITES
- HRI
- GM
- Ford
- OSU
- JPL
- NREL

* DOE EERE HFCIT Program Multi-year Plan for Storage

IEA HIA Task 32
Objectives

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

<table>
<thead>
<tr>
<th>Performance Measure</th>
<th>Units</th>
<th>2010</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>g H₂ /kg system</td>
<td>45</td>
<td>55</td>
<td>75</td>
</tr>
<tr>
<td>System Volumetric Capacity</td>
<td>g H₂ /L system</td>
<td>28</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>System fill time (for 5 kg H₂)</td>
<td>minutes</td>
<td>4.2</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Fuel Purity</td>
<td>% H₂</td>
<td></td>
<td></td>
<td>SAE J2719 guideline (99.97% dry basis)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Partner</th>
<th>S<em>M</em>A<em>R</em>T Milestone</th>
<th>Status</th>
</tr>
</thead>
</table>
| 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 L |
| UTRC    | NH₃ filter capable of 1800 miles fuel cell grade H₂ with a maximum mass of 1.2 kg and a maximum volume of 1.6 liters. | Demonstrated: 0.1 ppm NH₃  
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

| United Technologies Research Center | • MOF-5 risk assessment  
• Particulate mitigation |
|-------------------------------------|--------------------------|
| GM                                 | • Process development  
• BOP components  
• Testing of GLS with surrogate material  
• IRH-33 as support in NH₃ sorption filter  
• NH₃ filter performance tests  
• Risk assessment: AB flammability |
| Pacific Northwest National Laboratory | • Comparison of H₂ 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 |
| Los Alamos National Laboratory | |
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:
  - $N_2$ 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 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


<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Carryover in mass ppm</th>
<th>Average ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>603</td>
<td>724</td>
</tr>
<tr>
<td>170</td>
<td>7808</td>
<td>7189</td>
</tr>
</tbody>
</table>
GLS Model Development

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

  ![Diagram of GLS Model](image)

  - Gas: 600 slpm, Liquid: 0.72 slpm at 170°C
  - Knowledge gap: Droplet size distribution at GLS inlet

- Determined need for coalescence filter to remove small droplets

![Graphs showing droplet size distribution at 35 bar and 6 bar](image)

S*M*A*R*T:
- Gas: 600 slpm
- Liquid: 0.72 slpm at 170°C
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 MnCl₂ loading on super-activated carbon IRH-33 (UQTR) for dynamic adsorption of NH₃
- Develop and validate dynamic breakthrough adsorption model
- Size filter for 1800 miles
- Provide NH₃ filters of competitive adsorption test with ammonia + borazine mixtures to LANL

- Apply learning from evaluating particulate filters for cryo-adsorption system (<10 µm, <1 µg/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
Dynamic NH₃ Sorption Capacity

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

![Dynamic sorption capacity graph](chart.png)

- Developed and validated dynamic adsorption breakthrough model.

![NH₃ outlet/INlet vs Time graph](chart.png)

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

Ammonia Filter with 50 wt% MnCl₂ on IRH-33 meets weight and volume targets of HSECoE.
Minimizing NH₃ filter and H₂ gas cooler weight

<table>
<thead>
<tr>
<th>Radiator outlet temperature or Inlet temperature of adsorbent bed (°C)</th>
<th>Heat exchanger weight (kg)</th>
<th>Dynamic NH₃ sorption capacity (wt%)</th>
<th>NH₃ filter weight (kg)</th>
<th>Total weight (filter + Heat exchanger) (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.965</td>
<td>11.25</td>
<td>1.1</td>
<td>2.07</td>
</tr>
<tr>
<td>50</td>
<td>0.577</td>
<td>9.31</td>
<td>1.3</td>
<td>1.88</td>
</tr>
<tr>
<td>80</td>
<td>0.385</td>
<td>8.71</td>
<td>1.5</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Slight advantage of warm gas (80 °C) cleanup*.

(* Borazine filter components not yet included)
Technical Accomplishments and Progress

Framework with Graphical User Interface (GUI)

- Metal hydride storage system model example in Simulink® framework

### Hydrogen Vehicle Simulation Framework

**Select storage system**

- Metal hydride model (ORNL and SNL)

**Inputs**

- Zoomable plots
- Save results and generate Matlab® plots

**Results (at end of simulation)**

- H2 delivered: kg
- H2 used: kg
- Geometric capacity: %
- Volumetric capacity: g/L
- Temperature: °C
- Pressure: bar
- Fuel economy: mpg
- Range: miles
- Distance traveled: miles

**Stop simulation**

In beta test with ORNL and SNL.
Risk Assessment
(Comparison of solid AB versus liquid AB in terms of flammability)

Technical Accomplishments and Progress

**AB thermolysis in open air (inside ventilated hood)**
- Peak temperature during AB thermolysis in Air: \(196.1^\circ C\)
- Self-ignition of gases evolved from AB thermolysis in Air: \(89.7^\circ C\)
- Initial temperature: \(18.9^\circ C\)

**AB thermolysis in enclosed air (8.3 liters spherical test vessel)**
- Temperature peaked at: \(~273^\circ C\)
- Initial temperature: \(150^\circ C\)

**Slurry AB has similar ignition properties as solid AB.**

**10 wt. % AB Slurry**
- Peak temperature rise: \(213^\circ C\)
- Thermolysis off gases self-ignited at \(121^\circ C\)
- \(H_2\) ignition ignited the silicone oil

**AB slurry heating time [minutes]**

**AB powder heating time [minutes]**

**Peak temperature during AB thermolysis in Air: \(196.1^\circ C\)**

**Spark ignition initiated at \(~140^\circ C\)**

**Heating rate \(~1.6^\circ C/min\)**
Particulates
(SAE J2719 April 2008 Hydrogen Quality Guideline for FCV)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>ppm</th>
<th>Particulate size</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>5</td>
<td>&lt;10µm</td>
<td>&lt;1µg/L</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C1 basis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inert gases (N2, Ar)</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur compounds</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total halogenates</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total gases *</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen fuel index</td>
<td>&gt;99.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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™ 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)

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

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Questions and suggestions?
Technical Back-Up Slides
Publications and presentations


- 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*.


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

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 \( \text{H}_2 \), NH\(_3\) concentration 500 ppm
Absolute Pressure of hydrogen gas - 5 bar

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

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

Porosity = 30%
Average particle diameter = 800 \( \mu \text{m} \)

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.

- **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%).

Flexible screw auger
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

**Technical Accomplishments and Progress**