SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence
Design and Testing of Adsorbent Storage

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Overview

Timeline
- Start: February 1, 2009
- End: September 30, 2015
- 90% Complete (as of 3/1/14)

Budget*
- FY13 Funding: $1,030,000
- FY14 Funding: $1,400,000
- Total DOE Project Value $10,180,000

* Includes $240,000 for the Université du Québec à Trois-Rivières (UQTR) as a subrecipient for FY13/FY14 and funding for SRNL’s activities for HSECoE management.

Barriers
- A - System Weight and Volume
- C - Energy Efficiency
- E – Charging/Discharging Rates

Partners
Phase 3: 2013-2015

- Design, fabricate, test, and decommission the subscale prototype systems for adsorbent storage materials. **In Progress**

- Validate the detailed and system model predictions against the subscale prototype system to improve model accuracy and predictive capabilities. **In Progress**
Approach: FY2013 / FY2014 Milestones

SMART Milestones for SRNL/UQTR:

- Design and construct a hydrogen cryo-adsorbent test station capable of evaluating the performance of a two liter cryo-adsorbent prototype operating between 80-160K, which would meet all of the performance metrics for the DoE Technical Targets for On-Board Hydrogen Storage Systems. **In Progress**

- Design a 2L adsorbent subscale prototype utilizing a hex-cell heat exchanger storing 46g of available hydrogen, internal capacities of 0.13g/g gravimetric, and 23.4g/L volumetric. **Complete, Assembly in Progress**

- Update the cryo-adsorbent system model with Phase 3 performance data, integrate into the framework; document and release models to the public. Joint effort with NREL, PNNL, UTRC and Ford. **In Progress, Some Models Released**

Transport Phenomena Technology Milestones for SRNL/UQTR:

1. Refine the detailed models for scaled-up and alternative H$_2$ storage applications. **Complete**

2. Continue the FT cooling experiments, investigating MOF-5 powder, pellet, and compacted forms. Employ various HX concepts as applicable. **Complete**

3. Optimize the adsorbent system with respect to pressure work, enthalpy of H$_2$ discharge flow, dormancy conditions, and thermal interaction with the container well. **Complete**

4. Select an adsorbent, and form thereof, for use in the Phase 3 prototype. **Complete - Selected MOF-5**

5. Final design of a 2L hex-cell sub-scale adsorbent system. **Complete**

6. Complete test matrix for evaluation of the 2L hex-cell sub-scale adsorbent system. **In Progress**

7. Model validation for 2L hex-cell model against experiments. **In Progress**

8. Design, assemble and perform preliminary tests with the MATI heat exchanger. **Design in Progress**
Accomplishments: Performance With Respect to DOE Targets

End of Phase 1

End of Phase 2 Hex-Cell System

End of Phase 2 MATI System
Accomplishments: UQTR/SRNL Charging and Discharging Experiments

- Component level experiments for MOF-5 charging and discharging were conducted at UQTR
  - 0.5L vessel with hex-cell heat exchanger
  - Flow through cooling was used for the charging process
  - Heating via a resistive rod was used for the discharge process

- Phase III experimental components are being assembled at UQTR
  - 2L vessel with hex-cell heat exchanger
  - Test plan is in preliminary form

- Models developed/applied by SRNL replicate the experimental conditions
  - Purpose is validation of models against data to ensure predictive capability
    - Verify that physical processes are properly included/represented
Accomplishments: Chronology of UQTR Experiments

- **Small scale (0.5L vessel) experiments and models**
  - Purpose was to investigate component performance and validate models
  - MOF-5 flow-through cooling (charging) experiments
    - Discussed at previous AMR
  - Heating (discharge) experiments
    - Rig assembly – leak tests, heater behavior/characterization, hex-cell assembly
    - Tests with empty hex-cells
    - Tests with alumina filled hex-cells
    - Tests with MOF-5 powder
  - Model validation

- **Prototype (2L vessel) experiments and models**
  - Design and assemble:
    - Vessel and internal components
    - System components and test stand
  - Develop test Matrix
  - Conduct preliminary experiments and tests
  - Model validation
Accomplishments: Example of Component Issue
Power Distribution in Heating Cartridge and Redistribution by Hex-Cells

Heating Rod

- Manufacturer: Watlow®
- Max Power: 100 W
- Diameter: 0.6 cm
- Total Length: 25.4 cm
  (26.5 cm including connectors)
- Heated Length: 25.4 cm

Hex-Cells

- Manufacturer: Plascore®
- Flat-Flat distance: 0.6 cm
- Wall thickness: 0.01 cm
- 0.5 L Vessel
  - Section length: 2.54 cm
  - Total length: 25.4 cm (10 sections)
- 2 L Vessel
  - Section length: 10.0 cm
  - Total length: 20.0 cm (2 sections)

- Heating rod exhibits non-uniform power distribution
- Need to address in data evaluation & models
- Need to determine if hex-cell HX distributes thermal energy so rod can be approximated as having uniform or parabolic power
Accomplishments: 0.5L Hex-Cell Vessel Heating/Discharge Experiments

- **Empty hex-cells, no flow**
  - Vacuum
    - Room temperature at surface
  - 2.5 MPa hydrogen initially
    - Room temperature and 77K at surface

- **Filled hex-cells**
  - Alumina powder
    - 2.5 MPa hydrogen initially
    - No flow
  - MOF-5
    - 3.5 MPa hydrogen initially, room temp at surface, no flow
    - 3.5 MPa hydrogen initially, 77K at surface, no flow
    - 5.6 MPa hydrogen initially, 77K at surface, hydrogen outflow between 0 and 100 slpm*
    - 6.5 MPa hydrogen initially, 77K at surface, hydrogen outflow 25 slpm*

* reference T=21.1°C, P=1atm=101325 Pa
Accomplishments:
0.5 L Vessel Data and Model Comparison

MOF-5, Initially 3.5 MPa hydrogen, 77K at vessel surface, no outflow

- The hex-cell HX does distribute thermal energy
- Results shown for uniform heater power profile
  - Also good for parabolic power profile
Vessel, internals and test facility were designed and assembled
Can control cold hydrogen flowrate to 1000 splm for flow through cooling
Accomplishments: Installation of Heating Cartridge in Hex-Cell

Heating cartridge is 18cm long

- Single heater configuration was selected
  - Simpler installation
  - Requires fewer TC’s to monitor temperature profile
  - Can use symmetry in model
  - However, takes longer time to reach (160-170K)

0.5 L vessel tests indicated need for thermal isolation from tank wall

- A 0.125in thick Teflon® liner was used in the cylindrical section and in the domes of the tank

Heating cartridge is recessed by 0.8 inch (2cm) from the bottom hex-cell surface
Accomplishments: 3D Model Geometry for Hex-Cell Storage Vessel

- Geometry is in place
  - Replicates vessel and internals
- Model uses experimental BC’s
- Coupled to equations
- Will validate against data

- 2L tank in 3D geometry with 90° symmetry
- Leveraged previous experience for the 0.5L tank tests
- Model successfully running and preliminary tests are currently being modeled
First set of tests will be conducted without the hex cell structure inside the tank to check the actual characteristics of the tank (volume, etc.)

**Preliminary experimental tests to evaluate the actual performance of the heating rod (temperature profiles)**
- Tests will be repeated with empty cells and cells filled with alumina
  - Will use vacuum and pressurized H₂

**Flow through cooling/charging tests with MOF-5**
- Hydrogen flow rates up to 1000 SLPM
- Inlet H₂ at 80 K, inlet gas pressure ramp
- Test conditions:
  - Adsorption for LN₂ external temperature and max pressure
  - Adsorption with cooling and pressurization inside the tank (T=300-80K, P~0.3 - 70bar)
  - Additional sensitivity tests to be decided, based on initial results

**Heating/desorption tests with MOF-5**
- Room temperature at external surface, pressurized H₂, utilizing a suitable power ramp, with no hydrogen outflow
- External surface at LN₂ temperature, utilizing a suitable power ramp, with **no** H₂ outflow
- External surface at LN₂ temperature, utilizing a suitable power ramp, with **with** H₂ outflow

**Cycling tests charge-discharge-charge, etc.**
Accomplishments: Phase III  Planned MATI Prototype Design

- 2-Liter Type 1 6061-T6 Aluminum tank.
- Collared opening for full diameter access.
- 100 bar max working pressure

**Planned MATI design:**
- 10 cm diameter SS plates
- 8 to 10 ½-bed MATI sections
- 3.1 cm from cooling plate to cooling plate
- Mesh screen wrapping

**Planned data acquisition (TCs):**
- Profile along internal vessel wall
- Profile along 1 cooling plate
- Profile along external MOF surface
- 1 embedded TC per bed
- 1 heavily instrumented bed

**Planned Internal access to tank:**
- TC wires
- 2x N₂ lines
- 1x H₂ line
Accomplishments: P&ID for the SRNL MATI Prototype Test Facility

- **Gas supply:**
  - $\text{H}_2$ at 80 K and $>100$ slpm
  - $\text{LN}_2$ at $\sim7$ bar and 80 K
  - $\text{N}_2$ at $>373$ K and $>100$ slpm

- **System Data acquisition:**
  - P and T at all tank inlets/outlets
  - Mass flow control and measurements of all gas flows
Future Work: MATI Preliminary Test Plan

Initial Conditions
- System submerged within the LN$_2$ Dewar
- System is equalized to \(~77 \text{ K} – 80 \text{ K}\) at the **target pressure**
  - Target pressure of 60 bar (other pressures will be tested to verify system integrity)

Desorption
- Release H$_2$ from the pressure vessel at a fixed flow rate
- Simultaneously, run warm/hot gaseous N$_2$ through the MATI to induce desorption
  - Later testing may mimic driving conditions more closely by using a control scheme
- Continue desorption until the system reaches \(~5 \text{ bar}, \sim160 \text{ K} – 180 \text{ K}\)

Adsorption
- Begin adsorption immediately after desorption phase
  - Dependent on the as-built capabilities of the Prototype Test Facility
- Pressurize the vessel with H$_2$ at a fixed flow rate
- Simultaneously, run LN$_2$ through the MATI to induce adsorption
  - Later testing may mimic driving conditions more closely by using a control scheme
- Continue charging to \(~77 \text{ K} – 80 \text{ K}\) at the **target pressure**

Cycling... if possible
- If the system returns to near initial conditions, proceed directly to the next desorption cycle and perform at least 3 consecutive full cycles
Summary and Conclusions

- **Hex-Cell Heat Exchanger**
  - Small scale (0.5L) tests
    - Have experimentally validated hex-cell and resistance heater concept as means to discharge hydrogen
    - Models compare well with data
    - Non-uniform heater power represented well with parabolic or uniform profile

- **Phase III (2L) prototype**
  - Small scale tests and models were segue to Phase III
  - Phase III component set-up and configuration is underway at UQTR
    - Some tests performed with alumina in hex-cells
  - Numerical model framework for Phase III tests is in place
    - Equations and geometry are implemented

- **MATI Heat Exchanger**
  - Test facility
    - Phase III prototype design/construction is underway at OSU
    - The test facility is currently under construction at SRNL
      - Projected completion date of 01-July-2014
  - Models
    - Validation experiments to be conducted at SRNL
    - Numerical modeling will be performed by OSU
      - Model framework & guidance will be provided by SRNL
Internal Collaborations

Adsorbent Prototypes: Design, Testing and Model Validation

Modular Tank Insert: Optimization

H₂ Flow and Heat Exchanger: Modeling and Analysis

Flow-Through Heat Transfer Modeling

Compacted Media: Properties and Behavior

Pressure Vessels: Properties, Thicknesses, and “Thermos Design”

Adsorbent System Models
External Collaborations

- AIST
- Berkeley University
- Griffith University
- Curtin University
- International Energy Agency
- Max-Planck-Gesellschaft
- Savannah River National Laboratory
- HSECoE
Remaining Challenges and Barriers

- **Hex-Cell Experiments**
  - Models
    - Appropriate representation of physical processes
  - Thermocouples
    - Maintaining placement & location in adsorbent
    - Failure during tests
  - Internal Components
    - Adsorbent contact with heat exchanger wall
    - Adsorbent displacement
      - *May result in channeling or reduced contact with heat exchanger*

- **MATI Experiments**
  - Set up of test facility at SRNL
    - Shipment and installation of MATI
    - Proper functioning of components
    - Appropriate measurements for models
Responses to Previous Year Reviewers’ Comments

Comment: Paraphrasing similar comments by different reviewers; There is no consideration of the forecourt.

Response: DOE mandated that while the HSECoE must identify and report on the interface between the storage system and the forecourt in terms of mass and energy transfer (including pressures, temperatures, flowrates, etc.) the primary focus of the HSECoE is the storage system. Although recognized as an important issue, detailed forecourt analysis was specifically omitted from the tasks performed by the HSECoE.

Comment: It is unclear how the use of a Type-1 tank can lead to a go decision for Phase III. It is also unclear if this thermal mass can be cooled from 180 to 80 K in 3 minutes and what the penalty is in system efficiency due to this amount of cryogenic cooling.

Response: A Type-1 tank was selected for the prototype tests because: it was suitable for the 60-100 bar pressure range of the tests and was approximately half the cost of a Type-3 tank; it did not require a permeation liner as did the Type-3 tank. Calculations, discussed in prior meetings, indicated that the vessel could be charged via the flow-through cooling process, using 58 kg of LN2 to cool the vessel wall and re-cool the discharged hydrogen, in less than 3 minutes.

Comment: No interactions were mentioned with people and organizations outside of the Center.

Response: SRNL is using its experience with the HSECoE media based storage systems in the DOE SunShot and ARPA-E MOVE programs. Metal hydride models developed by the HSECoE are being used in collaborative efforts with Curtin and Griffith Universities in Australia as part of solar energy and solar generated hydrogen storage programs, respectively. Further, there is collaboration with AIST (Japan) and the IEA.

Comment: Because of the complex interactions and relationships with other teams it is difficult to judge the contributions of the SRNL/UQTR team.

Response: An effort has been made to clarify the SRNL/UQTR contributions in this presentation.
Technical Backup Slides
Flow-Through Cooling Adiabatic Wall & LN2 Assisted Cooling

A preliminary JPL test indicated that the time required to cool the outer wall is longer than assumed in the model (~1.5 minutes from 180 K to 80K). PNNL is currently conducting more detailed experiments.

### Temperature (K)

- $T_{0} = 180$ K
- $P_{0} = 5$ bar
- Ads Vol = 0.144m³
- Wall $\rho^{*}C_{p} = 2.43 \times 10^{6}$ (J/m³-K)

### Time to Charge (sec) | Total Mass of Exhaust $H_{2}$ (kg) | Total Exhaust $H_{2}$ Enthalpy (J)
---|---|---
200 Bar | 25 | 1.1 | $3.597 \times 10^{6}$
200 Bar Adiabatic | 101 | 11.4 | $1.641 \times 10^{7}$
60 Bar | 108 | 2.4 | $6.477 \times 10^{6}$
60 Bar Adiabatic | $>300$ | $>11.8$ | $>1.836 \times 10^{7}$

6.32 kg of Available Hydrogen is Stored At Full Charge.
Cost Analysis for Flow-Through Cooling

Model Assumes
- Saturated liquid nitrogen is boiled during cooling process
- Boiled nitrogen is vented (not reclaimed)
- Isentropic (adiabatic, reversible) \( \mathrm{H}_2 \) compression to inlet pressure followed by isobaric cooling to 80K

Time –Dependent Input from Finite Element Models
- Mass of available hydrogen
- Areal average exhaust pressure
- Enthalpy of exhaust hydrogen
- Rate of heat transfer from tank wall

Model Calculates
- Mass of nitrogen boiled to cool tank wall
- Mass of nitrogen boiled to cool compressed hydrogen
- Total cost of nitrogen boiled off

Filling a non-optimized 60 bar tank requires \( \sim 58 \text{kg} \) of saturated LN2
For a non-optimized 200 bar tank \( \sim 63 \text{kg} \) of saturated LN2 is required

Hydrogen is Reclaimed – Not Wasted
Flow Through Cooling is Reasonable Based on Mass of LN2 Required
Experimental Apparatus for LN2 Boundary Conditions

Liquid Nitrogen Bath

Pressure Vessel
Detailed Storage System Models

● Description

● Models couple:
  ● Conservation equations for mass, momentum and energy
  ● Equation of state for the gas
  ● Chemical kinetics and thermodynamic equations
  ● Other ancillary equations

● Any system, of any size, can be represented by the models by assigning appropriate geometry, components and boundary conditions

● Application

● Within the HSECoE, the detailed models have:
  ● Led the direction of the HSECoE program for metal hydrides and adsorbents
  ● Governed all important decisions regarding experiments, designs and storage system capability
  ● Predicted, in a general sense, results of experimental tests before they were conducted
    - This is why the models are used to select experimental designs having a high likelihood of meeting the technical targets
    - Experiments provide validation of model prediction and identify physical processes that improve resolution

● Use by other organizations

● Griffith University, Australia is using a form of the HSECoE metal hydride model to design storage facilities for 100 kg of solar-generated hydrogen

● The DOE SunShot program “Low-Cost Metal Hydride Energy Storage for Concentrating Solar Power,” in collaboration Curtin University, Australia, is using a form of the HSECoE metal hydride model to design thermal energy storage systems for concentrated solar power
MATI: Experiment / Model Validation Considerations

1. Uniform initial conditions
   - Let the system temperature and pressure equalize at known values prior to beginning the experiment.

2. Boundary conditions
   - The pressure vessel will be submerged within the LN$_2$ Dewar to provide an approximately uniform, constant temperature boundary temperature throughout the experiment.
   - The H$_2$ supply and pressurized LN$_2$ supply lines will be submerged within the LN$_2$ Dewar to supply feed gas at a temperature as close to 77K as possible.

3. Accurate measurement locations
   - Document the geometric location of all thermocouple locations for proper model validation.

The goal of the Phase 3 prototype testing is to validate the detailed models for predictive capabilities.
# MATI: Addressing DOE’s Technical Targets

<table>
<thead>
<tr>
<th>Target</th>
<th>2017 Value</th>
<th>Units</th>
<th>Measurement</th>
<th>Additional Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity</td>
<td>0.055</td>
<td>g&lt;sub&gt;H2&lt;/sub&gt; / g&lt;sub&gt;SYS&lt;/sub&gt;</td>
<td>Total Mass of Gas Stored</td>
<td>Total Mass of System (all equipment, tubing, tank, etc.)</td>
</tr>
<tr>
<td>Volumetric Capacity</td>
<td>40</td>
<td>g&lt;sub&gt;H2&lt;/sub&gt; / L&lt;sub&gt;SYS&lt;/sub&gt;</td>
<td>Total Mass of Gas Stored</td>
<td>Total Volume of System (all equipment, tubing, tank, etc.)</td>
</tr>
<tr>
<td>System Cost</td>
<td>12</td>
<td>$/kWh</td>
<td>Total Mass of Gas Stored</td>
<td>Total cost of the full experimental set-up</td>
</tr>
<tr>
<td>Fuel Cost</td>
<td>2-6</td>
<td>$/g&lt;sub&gt;gge&lt;/sub&gt;</td>
<td>Not Measured at SRNL/OSU</td>
<td></td>
</tr>
<tr>
<td>Ambient Temperature</td>
<td>-40 - 60 (sun)</td>
<td>°C</td>
<td>Room Temperature</td>
<td></td>
</tr>
<tr>
<td>Min/Max Delivery Temperature</td>
<td>-40 - 85</td>
<td>°C</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; Outlet Temperature</td>
<td></td>
</tr>
<tr>
<td>Operational cycle life (1/4 tank to full)</td>
<td>1500</td>
<td>cycles</td>
<td>Not Measured at SRNL/OSU</td>
<td></td>
</tr>
<tr>
<td>Min/Max Delivery Pressure</td>
<td>5 / 12 bar</td>
<td>bar</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; Outlet Pressure</td>
<td></td>
</tr>
<tr>
<td>On-board efficiency</td>
<td>90</td>
<td>%</td>
<td>Energy used to release the</td>
<td>Energy used to release the hydrogen (converted into H&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Wells-to-Power Plant Efficiency</td>
<td>60</td>
<td>%</td>
<td>Energy used to refuel / reload</td>
<td>Energy used to refuel / reload the hydrogen (converted into H&lt;sub&gt;2&lt;/sub&gt;)</td>
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<tr>
<td>System Fill Rate</td>
<td>1.5</td>
<td>kg&lt;sub&gt;H2&lt;/sub&gt; / min</td>
<td>Time to completely fill the tank (function of operating conditions)</td>
<td>Scaling this to our 2-Liter tank, it would only be a 4 second fill for the ~100 grams of H2</td>
</tr>
<tr>
<td>Min Full Flow Rate</td>
<td>0.02</td>
<td>(g/s)/kW</td>
<td>Not Measured at SRNL/OSU</td>
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<tr>
<td>Start time to full flow rate (20 °C)</td>
<td>5</td>
<td>s</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; Flow Rate?</td>
<td>Time to achieve full flow rate at start-up (no &quot;hold time&quot; listed)</td>
</tr>
<tr>
<td>Start time to full flow rate (-20 °C)</td>
<td>15</td>
<td>s</td>
<td>Not Measured at SRNL/OSU</td>
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<tr>
<td>Transient Response (10%-90% &amp; 90%-0%)</td>
<td>0.75</td>
<td>s</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; Flow Rate?</td>
<td>Time to achieve desired response in flow rate (&quot;driving&quot; response to rapidly accelerate and stop)</td>
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<tr>
<td>Fuel Purity (SAE J2719 &amp; ISO/PDTS 14687-2)</td>
<td>99.97</td>
<td>%&lt;sub&gt;H2&lt;/sub&gt;</td>
<td>Gas composition (via mass spec or RGA)</td>
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<td>Permeation &amp; Leakage</td>
<td>Scch/h</td>
<td>Not Measured at SRNL/OSU</td>
<td>Dust cloud ignition at BASF and/or UTRC</td>
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<tr>
<td>Toxicity</td>
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<td>Design for applicable safety standards</td>
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<tr>
<td>Safety</td>
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<td></td>
<td>Simplified thermos bottle + MLVI system TBD</td>
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