IV.B.1 Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

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Project End Date: September 30, 2018

Overall Objectives

- Coordinate the public access of select models developed under the Hydrogen Storage Engineering Center of Excellence (HSECoE) activity, including web posting of documentation and tracking downloads and web activity.
- Maintain performance of existing storage system models and update and validate as new experimental data becomes available.
- Enhance and expand existing models to improve simulation speed and application to other uses. This will focus on expanding the parameterization of the models and their flexibility in evaluating new material candidates. This will initially include the development of pre-processor sizing routines for the adsorbent and chemical hydrogen systems followed by the metal hydride and cryo-compressed systems.

Fiscal Year (FY) 2017 Objectives

- Coordinate the public access of selected HSECoE models, including web posting of documentation and tracking downloads and web activity.
- Develop a stand-alone isotherm data fitting routine to convert raw excess adsorption hydrogen data into its Dubinin-Astakhov (D-A) parameters.
- Graphical user interface (GUI) update for user input capability and update storage system model web site documentation and manuals.
- Develop stand-alone system estimator: executable version of the sizing functions for adsorbent and chemical hydrogen (CH) storage system models to create first-order storage system estimates based on material properties.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(E) Charging/Discharging Rates

(I) Dispensing Technology

(K) Systems Life-Cycle Assessments

Technical Targets

This project is conducting simulation and modeling studies of advanced onboard materials-based hydrogen storage technologies. Insights gleaned from these studies are being applied toward the hydrogen storage vessel design and materials synthesis that meet the following DOE 2020 hydrogen storage for light-duty vehicle targets.

- Storage system cost: \$333/kg $H_{2\ Stored}$
- System gravimetric capacity: 0.045 kg H_2/kg system
- System volumetric capacity: 0.030 kg H_2/L system
- Charging/discharging rates (5.6 kg H_2): 5 min
- Well to power plant efficiency: 60%

FY 2017 Accomplishments

- Completed a stand-alone isotherm data fitting routine to convert raw excess adsorption hydrogen data into its D-A parameters.
- Completed the update to the GUI for user input capabilities with documentation and updated the vehicle framework to add more user controls:
  - User can modify the chemical hydrogen material properties through the GUI in the chemical hydrogen storage system model.
- Completed the executable stand-alone system design tools for both the adsorbent and chemical hydrogen systems.
- Completed documentation updates for the posted models (including website text and downloadable user manual).
- Updated the website:
  - Added links to publications/abstracts.
  - Added relevant publications.
  - Moved vehicle framework section to the top and open by default.
- Troubleshooting of compiler and software versions.
- Tracked and monitored web activity and downloads.

INTRODUCTION

Overcoming challenges associated with onboard hydrogen storage is critical to the widespread adoption of hydrogen-fueled vehicles. The overarching challenge is identifying a means to store enough hydrogen onboard to enable a driving range greater than 300 miles within vehicle-related packaging, cost, safety, and performance constraints. As new hydrogen storage materials are discovered and created, material developers must predict their full-scale vehicle performance and compare their performance with pure hydrogen storage (700 bar, cryo-compressed, and liquid H_2 storage). The goal of this work is to provide material developers with the modeling tools necessary to make these predictions based on the work done by the HSECoE.

APPROACH

The approach for FY 2017 is to complete updates, validate, enhance, troubleshoot, de-bug and document these models developed by the HSECoE so that they can be made accessible to and useful for other research within the hydrogen storage community. During subsequent years, these models will be updated with alternative storage system formulations, such as different isotherm models for adsorbents and alternative chemical reaction kinetic expressions for CHs. In addition, stand-alone system estimators that do not require special software will be developed to serve as a scoping tool for the new hydrogen storage materials that may be developed.

RESULTS

The following provides results from work completed this year with a focus on the coordination of the public access of select HSECoE models, including web posting of documentation and tracking downloads and web activity. The multi-lab team worked on the validation, refinement, GUI improvements, troubleshooting, and improving the simulation run time of the models. They also updated model documentation for selected web postings and monitored/tracked web activity and model downloads. To date there have been 164 downloads of the tank volume/cost model, 113 downloads of the framework model, 77 downloads of the metal hydride (MH) finite element model, and 47 downloads of the MH acceptability envelop.

A stand-alone isotherm data fitting routine was developed to convert raw excess adsorption hydrogen storage data into its D-A isotherm parameters. Based on the original isotherm data fitting codes developed by SRNL and the Université du Québec à Trois-Rivières, this data fitting routine takes the raw excess adsorption data along with the hydrogen properties and fits them to the D-A isotherm model. The fitting routine has a usable data range of 20 K < T < 400 K and 0.05 MPa < P < 72 MPa. The fitting routine was tested using several sets of MOF-5 and AX-21 excess adsorption data and was found to match the original HSECoE fitting routine results. These D-A parameters are used within several of the computational models, including the Simulink vehicle model framework. By allowing material developers to fit their excess adsorption data using a standard fitting routine like this one, they can more easily utilize the computational models being developed and updated through this work, including the standalone system size estimator and the full-scale vehicle framework model.

The current stand-alone isotherm data fitting routine has been completed using Mathcad®, but the team is continuing to work on the fitting routine next year with the plan of converting it into a MATLAB® script and, if possible, convert it into a stand-alone executable.

Also during this year, both PNNL and SRNL completed stand-alone executable storage system design tools for the chemical hydrogen and adsorbent material systems, respectively. These system design tools bridge the gap between the material properties as measured by hydrogen storage material developers and the information needed for the framework model to demonstrate that a material does or does not meet the DOE Technical Targets for light-duty vehicles.

Chemical Hydrogen Storage System Design Tool

The chemical hydrogen system design tool requires the reaction parameters, the hydrogen capacity, and the mass and thermal properties of a hydrogen storage material. The tool then estimates the size of the individual components that feed into the hydrogen storage model, and the control parameters required to successfully run the storage model within the framework. The total system mass and volume are also estimated and can be used to determine if a particular material is worth further consideration. If the material appears to provide reasonable gravimetric and volumetric system densities, the individual components sizes and control parameters can then be used in the framework for each of the four drive cycles and the onboard efficiency and range can be determined.

The system design tool is written in MATLAB and can be run separate from the framework or can be run as a GUI within the framework as shown in Figure 1. After the vehicle framework is opened, the GUI includes the option to change the material/design. This button opens a separate worksheet that allows the user to modify existing material properties and operating conditions and then run the system design tool to provide updated design parameters that can then replace the defaults in the framework.

This system design tool can also be run as an executable file for which the inputs are brought into the function using a user-selected Excel spreadsheet. The results of the model are then written as a separate output spreadsheet. By developing an executable file, no MATLAB license is required. Instead a free downloadable program called MATLAB Runtime is used to run the executable file and provide the results. This approach will allow materials researchers that are not familiar with and/or do not have MATLAB and Simulink to evaluate their materials and obtain estimates of system mass and volume for preliminary comparison to the DOE Technical Targets.

Chemical hydrogen storage model kinetics were originally based on an Avrami expression with either a single reaction or two independent, parallel reactions. The system design tool has been expanded to also consider n^{th} order reaction kinetics as well. In this case, the kinetics are

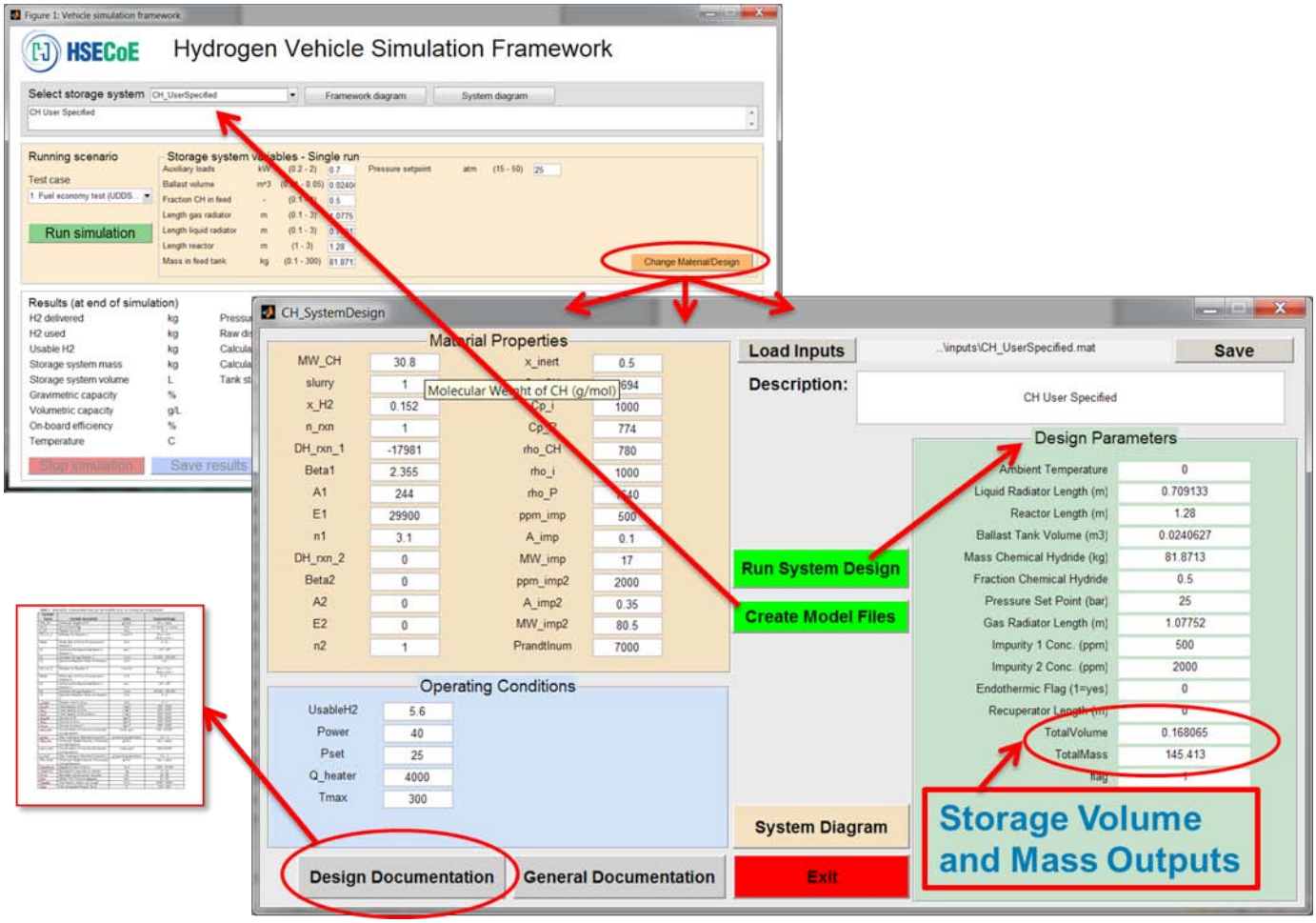


FIGURE 1. GUI format for the system design tool and its interaction with the Hydrogen Vehicle Simulation Framework

described as two series reactions of the form $A \rightarrow B + \beta_1 H_2 \rightarrow C + \beta_2 H_2$. This new analysis is described by the following kinetic expressions:

$$\left.\frac{\partial \alpha_1}{\partial t}\right|_{kinetics} = k_1\left[C_0(1-\alpha_1)\right]^{n_1} \qquad \left.\frac{\partial \alpha_2}{\partial t}\right|_{kinetics} = k_2\left[C_0(\alpha_1-\alpha_2)\right]^{n_2}$$

Two materials are included within the framework and have been used to exercise the system design tool. The first is ammonia borane, which is an example exothermic material. The second is alane, which is an example endothermic material. These are both modeled with the Avrami kinetic expression that was the initial kinetics expression within the vehicle framework. A carbon-boron-nitrogen (CBN) compound, 1,2 BN cyclohexane, is examined to evaluate the n^{th} order kinetic model. The kinetics and thermodynamics of these materials are provided as input, while their output is shown in Table 1 below. The pure CBN material, which is a liquid, has a much smaller volume and mass than the other two materials that require 50% dilution to create a slurry. The CBN compound has an exothermic and an endothermic reaction in series.

TABLE 1. Calculated Chemical Hydrogen Parameters from the System Design Tool

Calculated System Parameter	Ammonia Borane	Alane	CBN
Total System Mass (kg)	133	188	117
Total System Volume (L)	146	161	135
System Gravimetric Capacity (kg H_2/kg system)	0.042	0.029	0.048
System Volumetric Capacity (kg H_2/L system)	0.038	0.035	0.041
Reactor Length (m)	0.64	1.28	2.3
Ballast Tank Volume (L)	14	22	32
Mass Chemical Hydride (kg)	77	128	70
Fraction Chemical Hydride	0.5	0.5	1
Liquid Radiator Length (m) (3 tubes)	2.4	1.6	0.9
Gas Radiator Length (m) (1 tube)	1.2	1.0	1.4
Recuperator Length (m) (3 tubes)	0	3.22	0.8
Startup Temperature (°C)	178	202	279
Ballast Time(s)	75	117	176

Adsorbent Hydrogen Storage System Design Tool

Similar to the chemical hydrogen design tool, the adsorbent hydrogen storage system design tool is MATLAB script that is both a part of the hydrogen vehicle simulation framework and an individual stand-alone executable design tool. It estimates the hydrogen storage system details, including the mass and volume, as well as the details of the individual components based on the material properties and the operating conditions. Note that the user cannot currently control the adsorbent materials properties within the GUI interface of the vehicle simulation framework, but this control will be included in the vehicle framework next year.

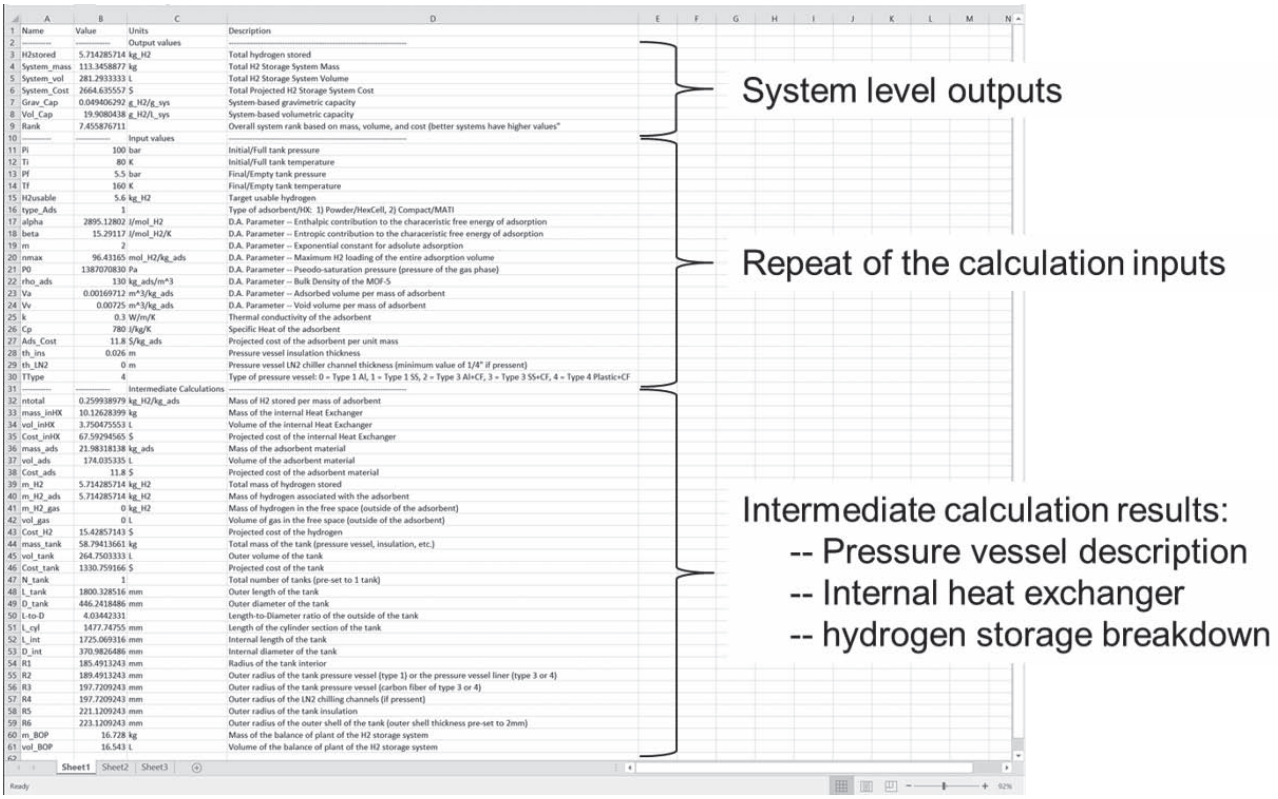
When running the stand-alone executable version of the adsorbent storage system design tool, the inputs are read into the script using a user-selected pre-formatted Excel spreadsheet, while the results are written to a separate spreadsheet. The user has full control over the operating conditions within 40 K < T < 400 K and 5.0 bar < P < 720 bar, but the user is limited to the operating conditions covered by the user's isotherm data that was used to create the materials properties. The adsorbent material's hydrogen properties must be converted into its D-A parameters, including the void volume. The user can also include the material's thermal properties and input an estimated cost. Finally, the user can choose other system-specific design parameters, such as the type of pressure vessel, the insulation thickness, and the adsorbent condition (either powder or compacted adsorbent). An example of the resulting output file for powder MOF-5, which includes the input parameters used to perform the calculation, is shown in Figure 2.

Several materials were used to test the executable stand-alone adsorption system design tool, including several forms of MOF-5 and activated carbon. Representative results of these materials are shown in Table 2. Note that the following design assumptions were used to make Table 2.

- Operating conditions: 80 K, 100 bar with swing to 160 K, 5 bar
- 5.6 kg of usable hydrogen (~5.714 kg of actual hydrogen storage)
- Type 1 aluminum pressure vessel
- LN_2 pressure vessel chiller channel thickness of 9.525 mm
- Uniform insulation thickness of 23 mm, with a 2 mm outer aluminum shell

Documentation has been completed for the stand-alone executable storage system design tools for the chemical hydrogen and adsorbent material systems, respectively. These system design tools bridge the gap between the material properties as measured by hydrogen storage material developers and the information needed for the framework model to demonstrate that a material does or does not meet the DOE Technical Targets for a light-duty vehicle. These stand-alone models, which include their documentation, are now accessible from the http://hsecoe.org website under model downloads (Table 3).

The Hydrogen Vehicle Simulation Framework model has been updated along with its documentation showing the added capability to design a storage system for the CH and adsorbent systems. Users can now access design parameters



	Name	Value	Units	Description
2	----------	----------	Output values	----------
3	H2stored	5.714285714	kg_H2	Total hydrogen stored
4	System_mass	113.3458877	kg	Total H2 Storage System Mass
5	System_vol	281.2933333	L	Total H2 Storage System Volume
6	System_Cost	2664.635557	$	Total Projected H2 Storage System Cost
7	Grav_Cap	0.049406292	g_H2/g_sys	System-based gravimetric capacity
8	Vol_Cap	19.9080438	g_H2/L_sys	System-based volumetric capacity
9	Rank	7.455876711		Overall system rank based on mass, volume, and cost (better systems have higher values"
10	----------	----------	Input values	----------
11	Pi	100	bar	Initial/Full tank pressure
12	Ti	80	K	Initial/Full tank temperature
13	Pf	5.5	bar	Final/Empty tank pressure
14	Tf	160	K	Final/Empty tank temperature
15	H2usable	5.6	kg_H2	Target usable hydrogen
16	type_Ads	1		Type of adsorbent/HX: 1) Powder/HexCell, 2) Compact/MATI
17	alpha	2895.12802	J/mol_H2	D.A. Parameter -- Enthalpic contribution to the characeristic free energy of adsorption
18	beta	15.29117	J/mol_H2/K	D.A. Parameter -- Entropic contribution to the characeristic free energy of adsorption
19	m	2		D.A. Parameter -- Exponential constant for adsolute adsorption
20	nmax	96.43165	mol_H2/kg_ads	D.A. Parameter -- Maximum H2 loading of the entire adsorption volume
21	P0	1387070830	Pa	D.A. Parameter -- Pseodo-saturation pressure (pressure of the gas phase)
22	rho_ads	130	kg_ads/m^3	D.A. Parameter -- Bulk Density of the MOF-5
23	Va	0.00169712	m^3/kg_ads	D.A. Parameter -- Adsorbed volume per mass of adsorbent
24	Vv	0.00725	m^3/kg_ads	D.A. Parameter -- Void volume per mass of adsorbent
25	k	0.3	W/m/K	Thermal conductivity of the adsorbent
26	Cp	780	J/kg/K	Specific Heat of the adsorbent
27	Ads_Cost	11.8	$/kg_ads	Projected cost of the adsorbent per unit mass
28	th_ins	0.026	m	Pressure vessel insulation thickness
29	th_LN2	0	m	Pressure vessel LN2 chiller channel thickness (minimum value of 1/4" if pressent)
30	TType	4		Type of pressure vessel: 0 = Type 1 Al, 1 = Type 1 SS, 2 = Type 3 Al+CF, 3 = Type 3 SS+CF, 4 = Type 4 Plastic+CF
31	----------	----------	Intermediate Calculations	----------
32	ntotal	0.259938979	kg_H2/kg_ads	Mass of H2 stored per mass of adsorbent
33	mass_inHX	10.12628399	kg	Mass of the internal Heat Exchanger
34	vol_inHX	3.750475553	L	Volume of the internal Heat Exchanger
35	Cost_inHX	67.59294565	$	Projected cost of the internal Heat Exchanger
36	mass_ads	21.98318138	kg_ads	Mass of the adsorbent material
37	vol_ads	174.035335	L	Volume of the adsorbent material
38	Cost_ads	11.8	$	Projected cost of the adsorbent material
39	m_H2	5.714285714	kg_H2	Total mass of hydrogen stored
40	m_H2_ads	5.714285714	kg_H2	Mass of hydrogen associated with the adsorbent
41	m_H2_gas	0	kg_H2	Mass of hydrogen in the free space (outside of the adsorbent)
42	vol_gas	0	L	Volume of gas in the free space (outside of the adsorbent)
43	Cost_H2	15.42857143	$	Projected cost of the hydrogen
44	mass_tank	58.79413661	kg	Total mass of the tank (pressure vessel, insulation, etc.)
45	vol_tank	264.7503333	L	Outer volume of the tank
46	Cost_tank	1330.759166	$	Projected cost of the tank
47	N_tank	1		Total number of tanks (pre-set to 1 tank)
48	L_tank	1800.328516	mm	Outer length of the tank
49	D_tank	446.2418486	mm	Outer diameter of the tank
50	L-to-D	4.03442331		Length-to-Diameter ratio of the outside of the tank
51	L_cyl	1477.74755	mm	Length of the cylinder section of the tank
52	L_int	1725.069316	mm	Internal length of the tank
53	D_int	370.9826486	mm	Internal diameter of the tank
54	R1	185.4913243	mm	Radius of the tank interior
55	R2	189.4913243	mm	Outer radius of the tank pressure vessel (type 1) or the pressure vessel liner (type 3 or 4)
56	R3	197.7209243	mm	Outer radius of the tank pressure vessel (carbon fiber of type 3 or 4)
57	R4	197.7209243	mm	Outer radius of the LN2 chilling channels (if pressent)
58	R5	221.1209243	mm	Outer radius of the tank insulation
59	R6	223.1209243	mm	Outer radius of the outer shell of the tank (outer shell thickness pre-set to 2mm)
60	m_BOP	16.728	kg	Mass of the balance of plant of the H2 storage system
61	vol_BOP	16.543	L	Volume of the balance of plant of the H2 storage system

FIGURE 2. Executable stand-alone adsorbent system design tool output for powder MOF-5

TABLE 2. Representative Results from the Adsorbent Hydrogen System Design Tool

	Gravimetric Capacity [g_{H2}/g_{sys}]	Volumetric Capacity [g_{H2}/L_{sys}]	Source
MOF-5 Powder [130 kg/m^3]	0.0339 g/g	18.6 g/L	HSECoE
MOF-5 Compact [406 kg/m^3]	0.0314 g/g	21.4 g/L	HSECoE
DUT-23 (Co) Powder* [200 kg/m^3]	0.0348 g/g	20.7 g/L	Ford/Univ. of Michigan
IRMOF-20 Powder* [200 kg/m^3]	0.0341 g/g	20.3 g/L	Ford/Univ. of Michigan
MOF-5 Powder [200 kg/m^3]	0.0332 g/g	19.6 g/L	HSECoE

*Special thanks to Ford and the University of Michigan for sharing their data.

and material properties to input their own storage systems from the main GUI of the framework or work with the stand-alone models mentioned previously.

The models are available publicly through the HSECoE web page, where web site activity and model down loads are tracked. Figure 3 shows the latest web site activity over the three month period from April to June, 2017. The site received over 200 visitors during this time, with roughly 50% of those being new visitors. The bounce rate is 18%, indicating that 82% of the visitors browse further than the landing page, and have an average stay of over 5 min. Figures 4 and 5 provide the user flows for the site and user origin cities, respectively.

TABLE 3. HSECoE Models Available on Web Portal and Model Posting Status

Model Name	Lead	Status
MH Acceptability Envelop	SRNL	Complete
MH Finite Element Model	SRNL	Complete
Tank Volume/Cost Model	PNNL	Complete
MH Framework Model	SRNL	Complete
CH Framework Model	PNNL	Complete
Adsorption Data (AD) Framework Model	SRNL	Complete
AD Finite Element Model	SRNL	Model Complete*
Adsorption Data Fitting Routine	SRNL	Model Complete*
AD Stand-alone System Design Tool	SRNL	Complete
CH Stand-alone System Design Tool	PNNL	Complete

*Awaiting user's manual completion before the model is released to the public.

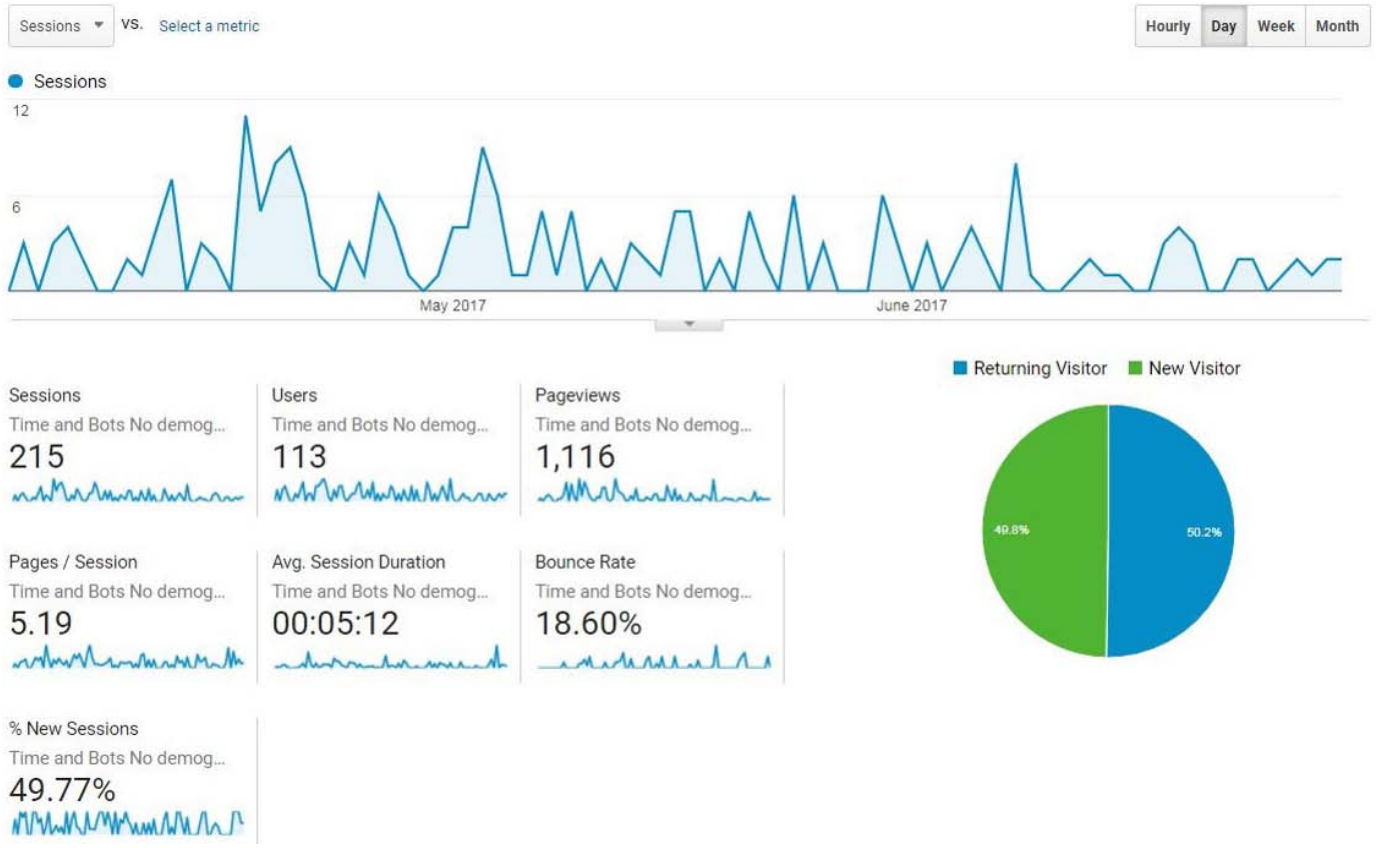


FIGURE 3. HSECoE web analytics: three month site activity metrics

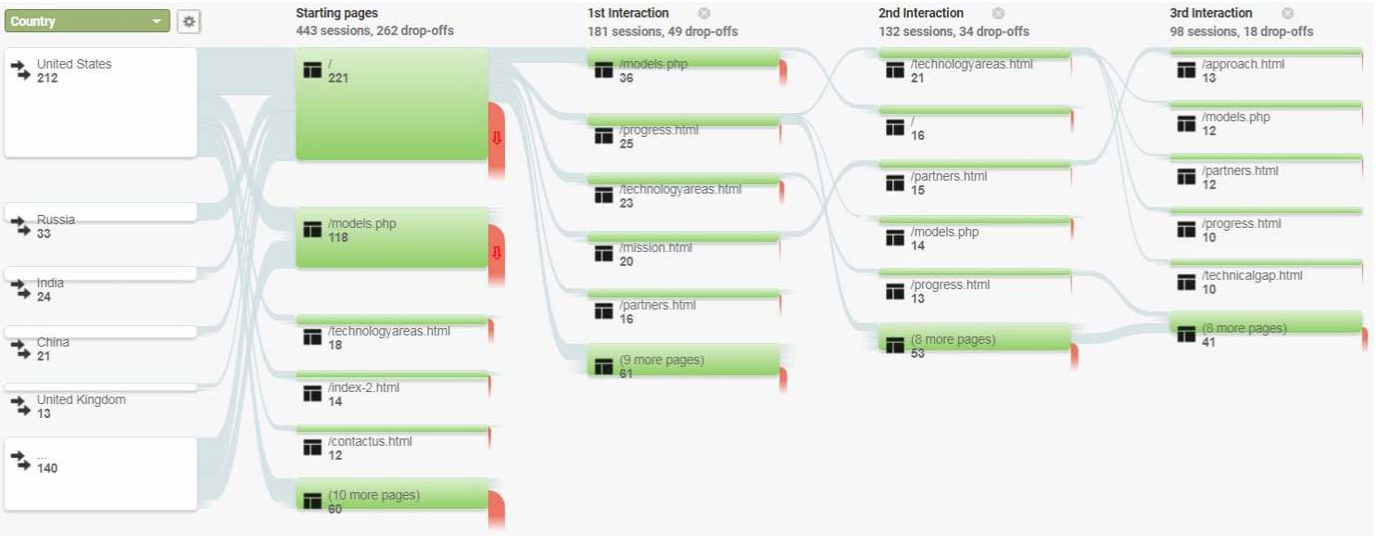


FIGURE 4. HSECoE web analytics: user flows

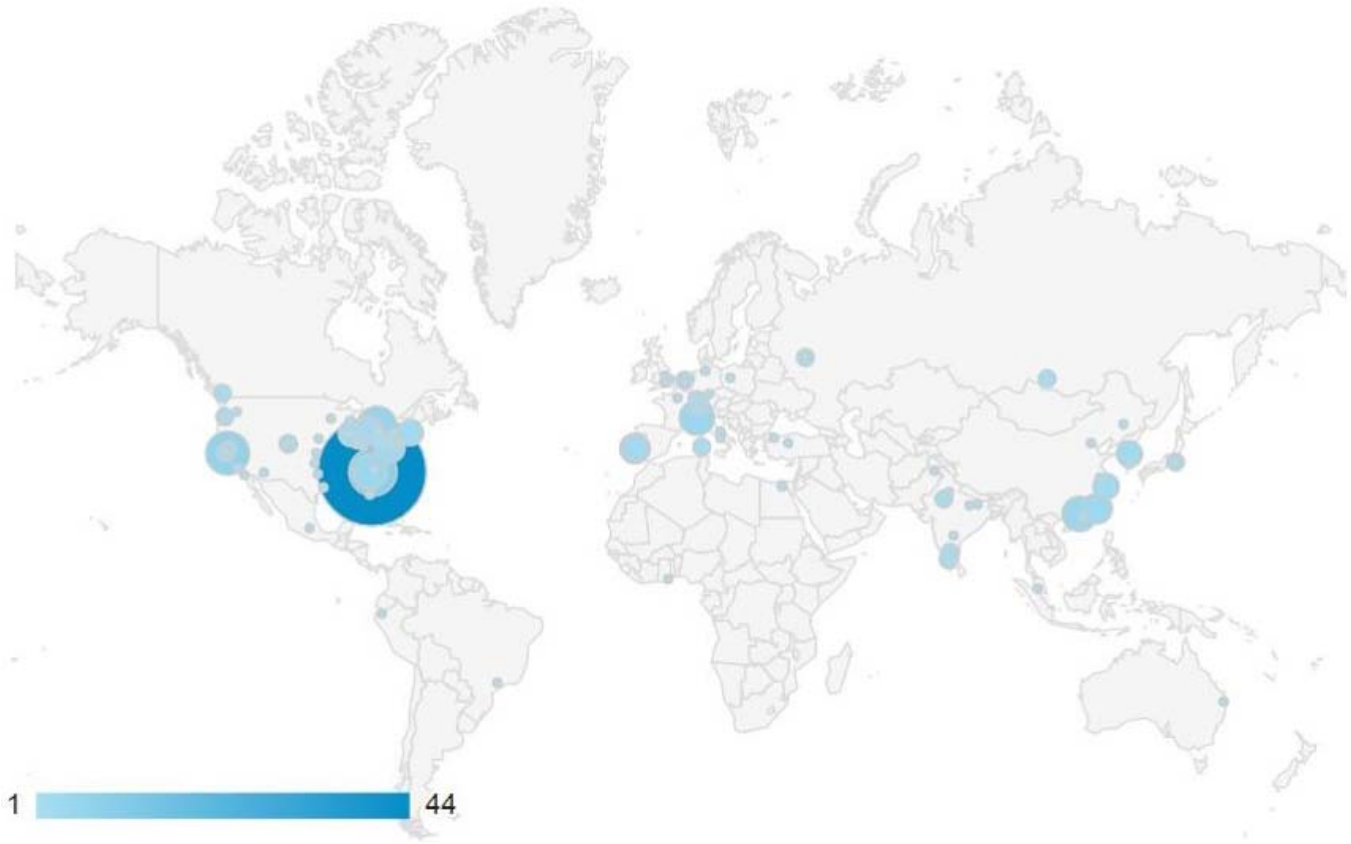


FIGURE 5. HSECoE web analytics: user origin countries

CONCLUSIONS AND UPCOMING ACTIVITIES

- Work with HSECoE partners to continue to update and improve center developed models. Make these models available and accessible to the broader research and academic community through a controlled web based access portal and track downloads and web site activity.
- Create stand-alone executable versions of the HSECoE developed material storage models to provide first-order storage system estimates based on material property information.
- Update the hydrogen storage equations with additional, alternative theoretical storage system formulations to allow users to choose the most appropriate theory for their material.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Thornton, M., D. Tamburello, K. Brooks, S. Sprik, "Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements," U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, June 8, 2017.

2. Thornton, M., D. Tamburello, K. Brooks, S. Sprik, "HSECoE Models on the WEB," Hydrogen Storage Technical Team Review, January 19, 2017.