High Efficiency Solar Thermochemical Reactor for Hydrogen Production

DOE Annual Merit Review

Project ID: PD113

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Sandia National Laboratories

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Timeline

- Project Start Date: 10/01/2014
- Project End Date: 09/30/2017*
- Project Complete: 99%

Barriers Addressed

- S: High-Temperature Robust Materials
- T: Coupling Concentrated Solar Energy and Thermochemical Cycles
- X. Chemical Reactor Development and Capital Costs

Budget

- Total Project Budget.
  - $3.343M
- Total Recipient Share.
  - $0.244M
- Total Federal Share.
  - $3.250M
- Total DOE Funds Spent:
  - $3.250M

Collaborators

- German Aerospace Center-DLR , Cologne DE.
- Arizona State University, Tempe AZ.
- Bucknell University, Lewisburg PA.
- Colorado School of Mines, Golden CO.
- Northwestern University, Evanston IL.
- Stanford University, Stanford CA.

*Contingent upon completion of FOA GNG.

Relevance

DOE Objective (2015 MYRDDP): Verify the potential for solar thermochemical (STCH) cycles for hydrogen production to be competitive in the long term and by 2020, develop this technology to produce hydrogen with a projected cost of $3.00/gge at the plant gate.

Table 3.1.13 Technical Task Descriptions			SNL Impact
Task	Description	Barriers	
4	High-Temperature, Solar-Driven, Thermochemical Processes • Optimize sub-cycle reactions and verify effective hydrogen production at laboratory scale. • Quantify and verify conversion efficiency and kinetics for reaction cycles. • Develop a viable integrated, solar-driven high-temperature thermochemical water-splitting process. • Verify an integrated, solar-driven high-temperature thermochemical water-splitting cycle with targeted costs. • Develop a solar field configuration and design to match chemical plant requirements. • Identify strategies for full integration of solar thermal energy collection and storage with the chemical reaction cycle for thermochemical water-splitting. • Verify performance of a semi-integrated system at small scale (5-100 kW). • Verify that a fully-integrated system can achieve 2020 targeted costs and yields.	S, T, X	• Quantified conversion efficiency and kinetics of novel STCH materials and derived insight into improving performance. • Developed a fully operational hydrogen producing reactor to verify system performance at ~5 kW. • Designed a central receiver based hydrogen production plant to investigate how a fully-integrated system can achieve 2020 targeted costs and yields.

Approach: Project Phases and Milestones

F15Q1 | F15Q2 | F15Q3 | F15Q4 | F16Q1 | F16Q2 | F16Q3 | F16Q4 | F17Q1 | F17Q2

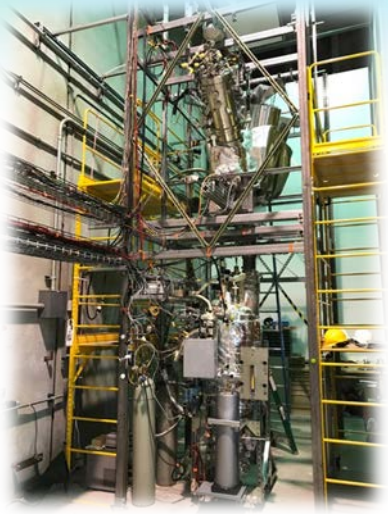
- Formulate and synthesize redox active oxides from $LaAlO_3$ (variants of La-Sr-Mn system). 100%
- Formulate and synthesize redox active oxides from earth abundant elements (AE, 3dTM) and explore methods for entropy engineering. 100%
- Acquire 150 kg of CeO_2 particles for CPR2 tests. 100%
- Characterize thermodynamic, kinetic, and other relevant properties of newly synthesized materials. 100%
- Design CPR2 and produce engineering drawings for fabrication. 100%
- Design and construct ~20kW$_{ele}$ solar simulator for CPR2 test. 100%
- Fabricate CPR2 components, procure non-custom components, execute staged buildout and testing plan. 99%*
- Develop mass and energy flow models of large scale H_2 production plant. One-dimensional, steady state models of discrete unit operations. 100%
- Conduct technoeconomic and trade-off analysis for STCH plant. 100%

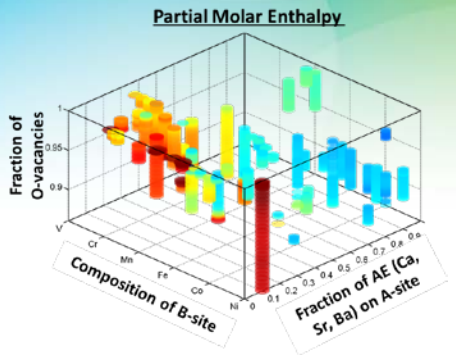
MATERIALS | REACTOR | ANALYSIS

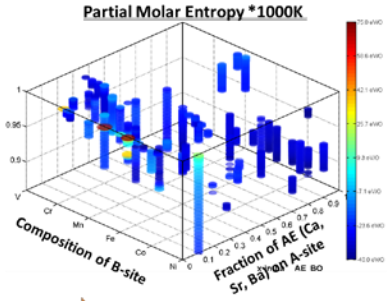
*Contingent upon completion of FOA GNG.

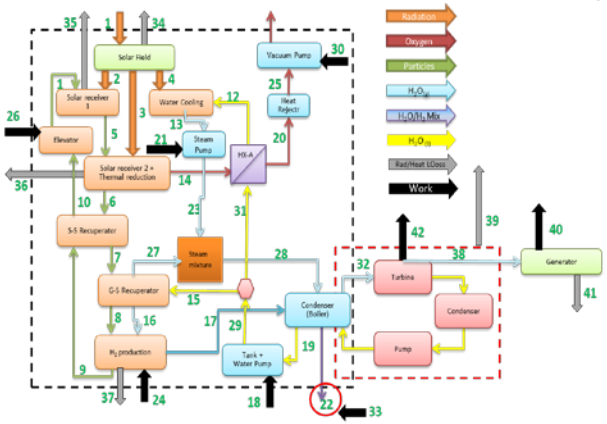
Approach: FY16-17 Objectives

- Discover and characterize select oxide materials for water-splitting cycles. (Barrier S & T)
- Construct and demonstrate a particle receiver-reactor capable of continuous operation at >3kW$_{th}$ thermal input. (Barrier T)
- Conduct technoeconomic and trade-off analysis of large-scale H_2 production facility using a plant-specific predictor model. (Barrier X)





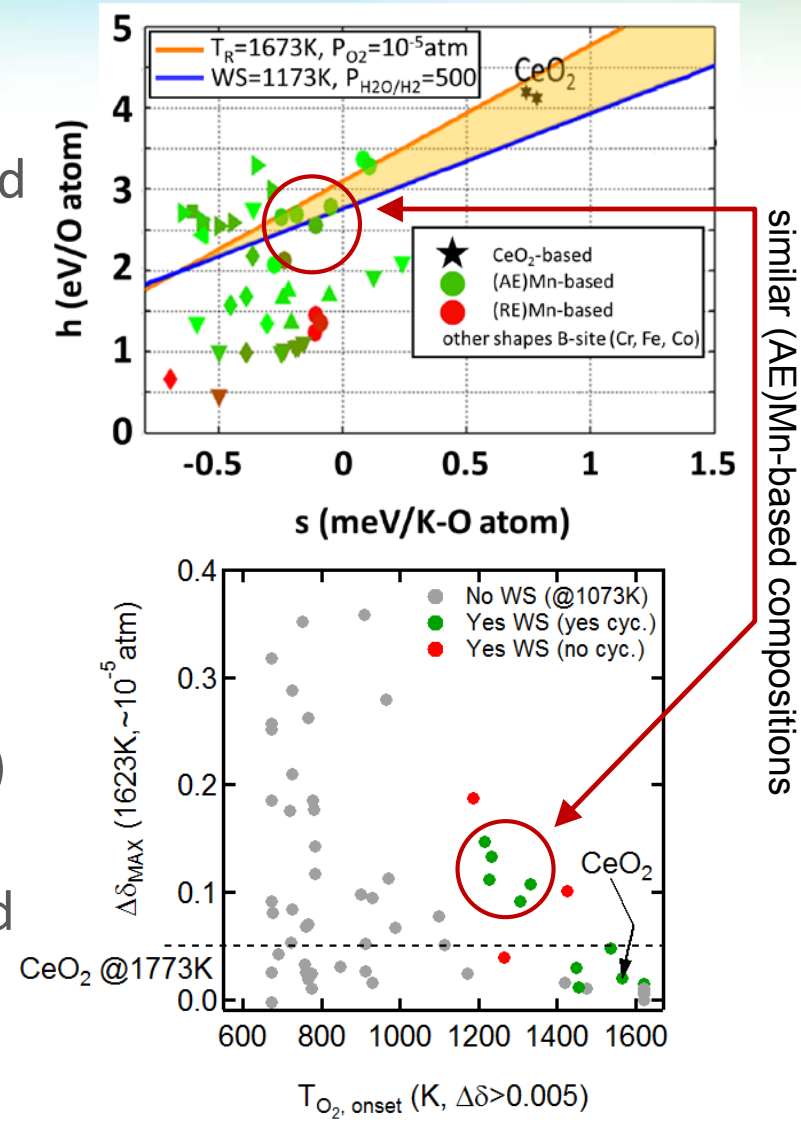




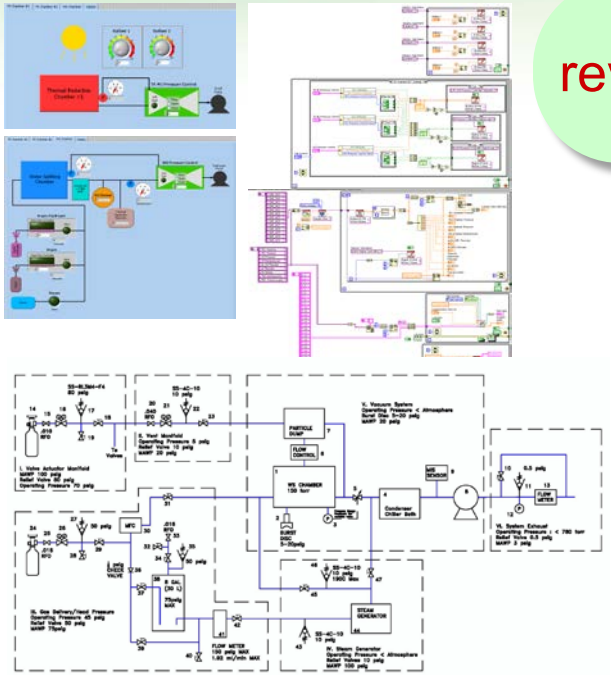
Advancing solar H_2 production through materials and engineering innovation.

Technical Accomplishments and Progress: Generated a Great Deal of STCH Materials Knowledge

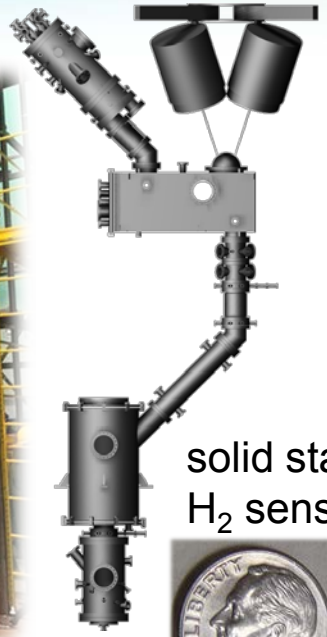
- Emerging perovskite design rules based on A-site and B-site compositions.
  - Exploited ΔH_R reduction trends reported in literature
  - Entropy engineering proving more difficult (no obvious trends)
- (AE, RE)Mn-based perovskites other than SLMA show promise.
  - Find balance between $\Delta\delta$ (H_2 capacity) and ΔH_R (lowering T_R)
- Exploiting complex crystallography and solid-solid phase transitions possible.
  - Double perovskites ($A_2BB'O_6$)



Technical Accomplishments and Progress: Completed CPR2 assembly



Engineering & Safety reviews complete, authorized for full operation.

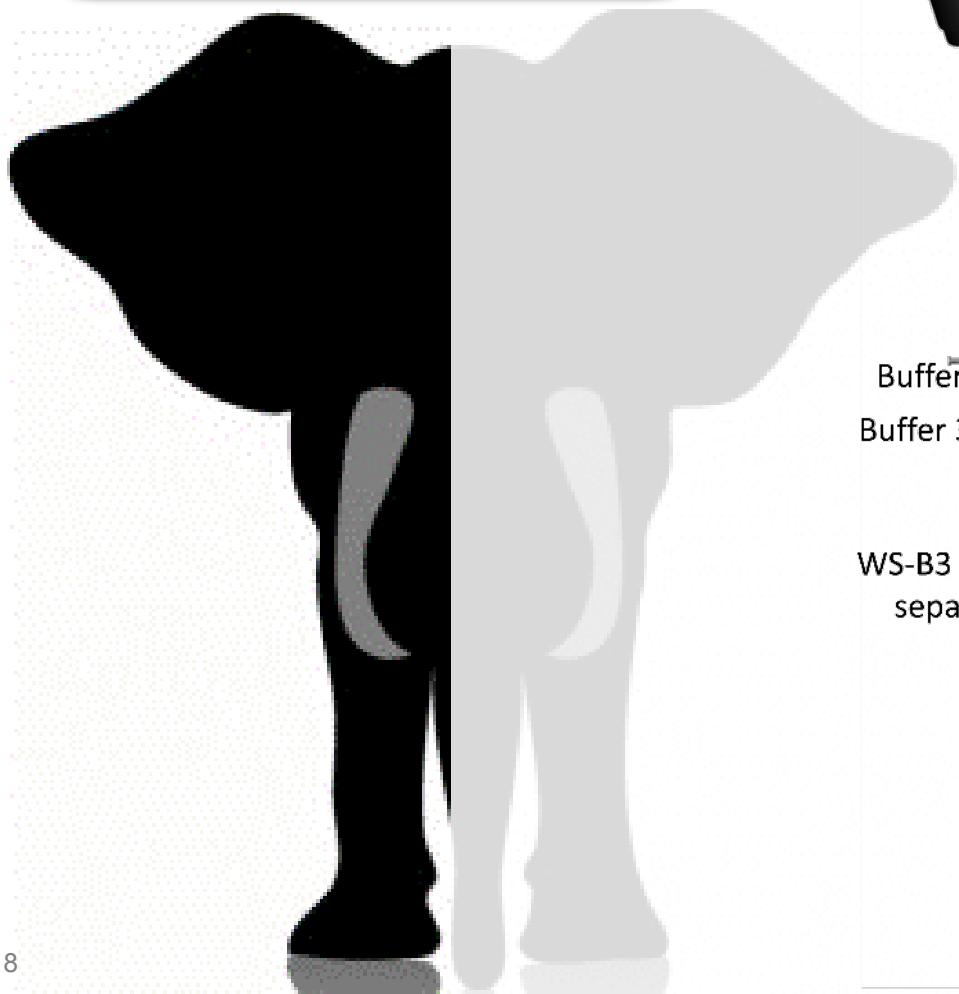


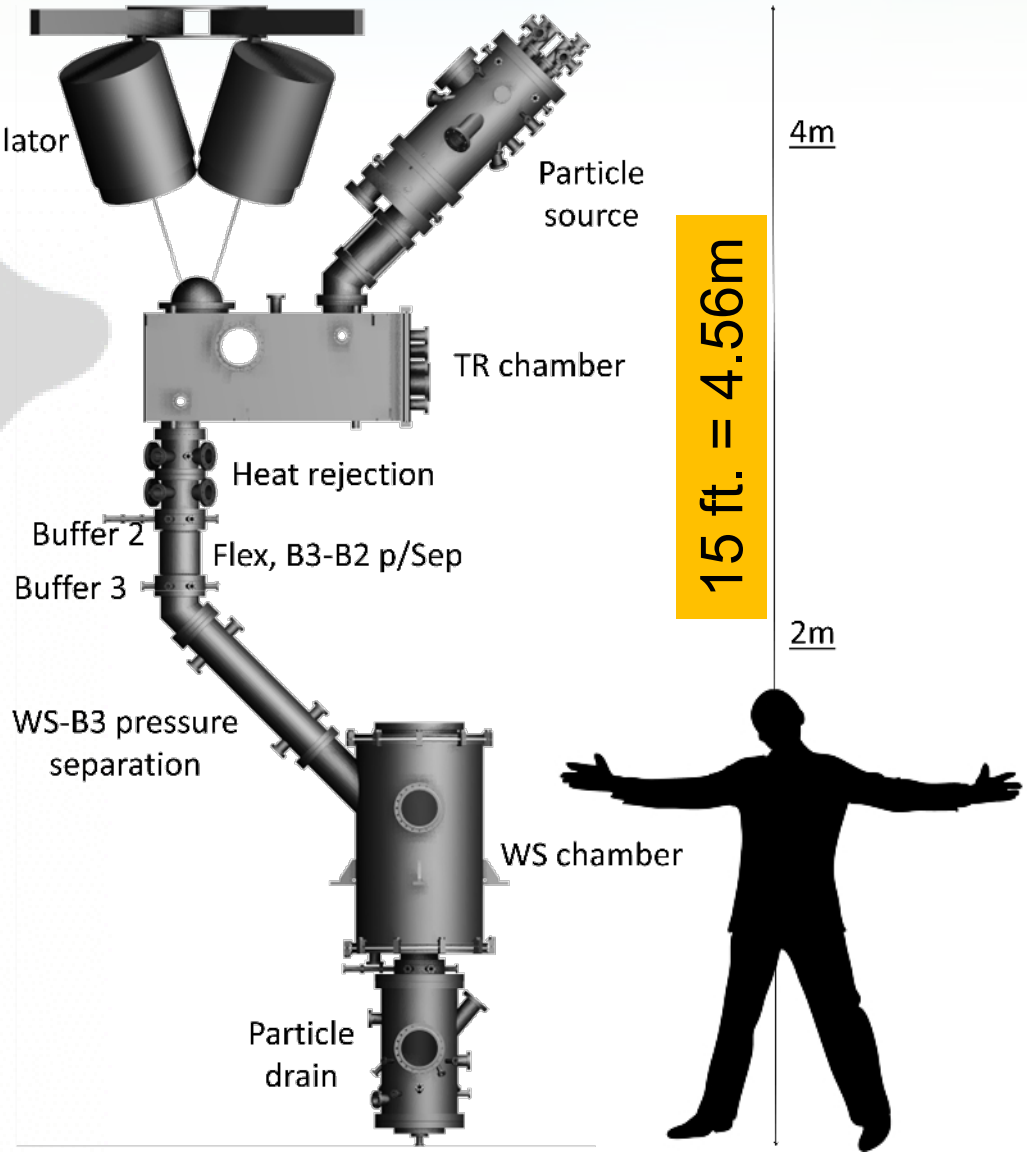
solid state H_2 sensor

- STCH hydrogen production reactor facility specifications:
  - Vacuum system with ~10 Pa (0.0001 atm) base pressure at 1700 K cavity temperature
  - 10.6 kW_{el}, four-lamp solar simulator (~3.4 kW_{th} at cavity aperture)
  - Instrumented with ~100 TC's, optical pyrometer, motorized particle flow control, gas flow and pressure sensing/control, Sandia's MIS H_2 sensor, CCTV system, etc.
  - DAQ is LabVIEW-based and provides measurement & control through custom GUI

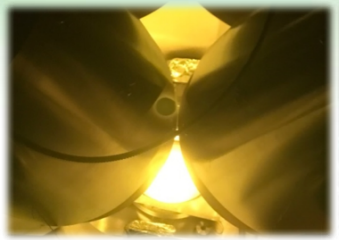
Technical Accomplishments and Progress: Scale of CPR2 assembly

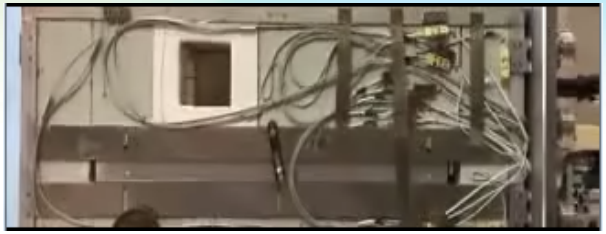
Bootstrapped a unique STCH research facility in less than 3 years.

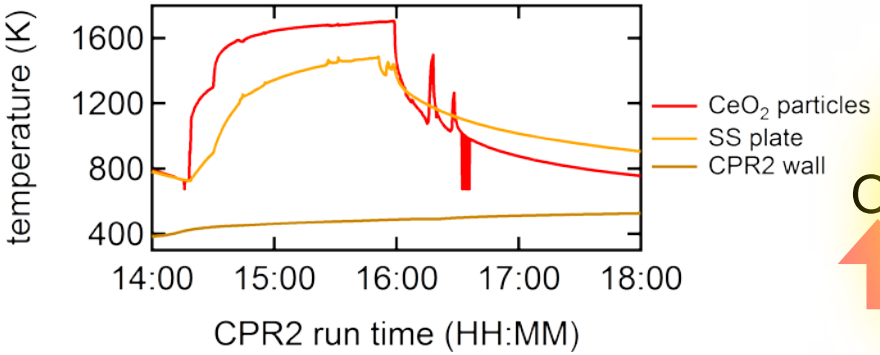


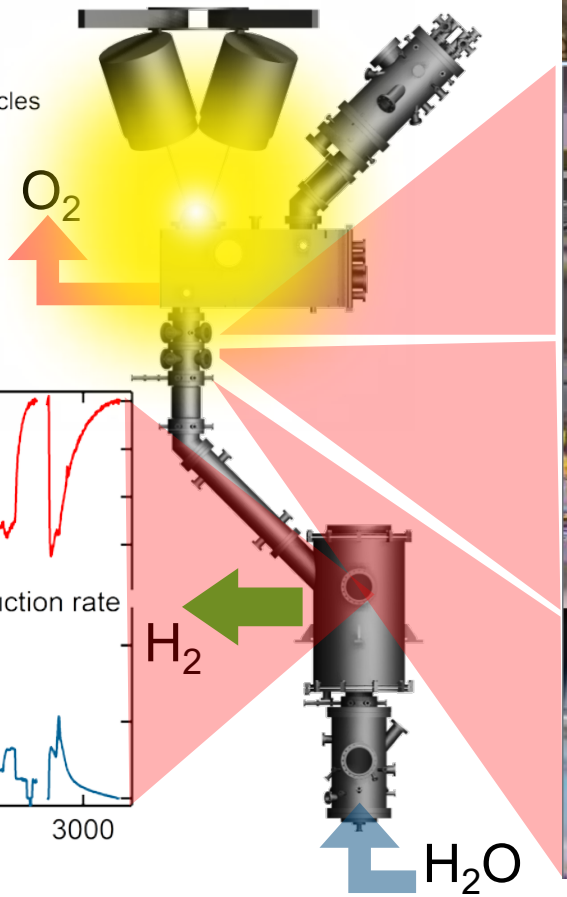


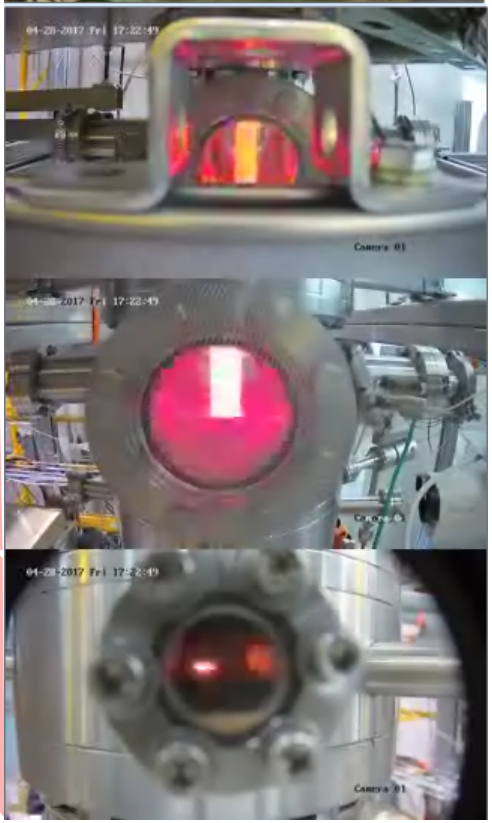
Technical Accomplishments and Progress: Achieved H_2 production







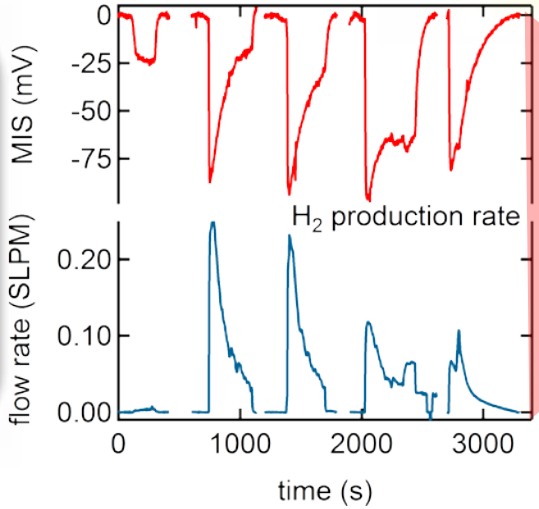




T_R~1700 K.

0.25 SLPM peak H_2 rate.

Can achieve FOA GNG in <<8 hrs.

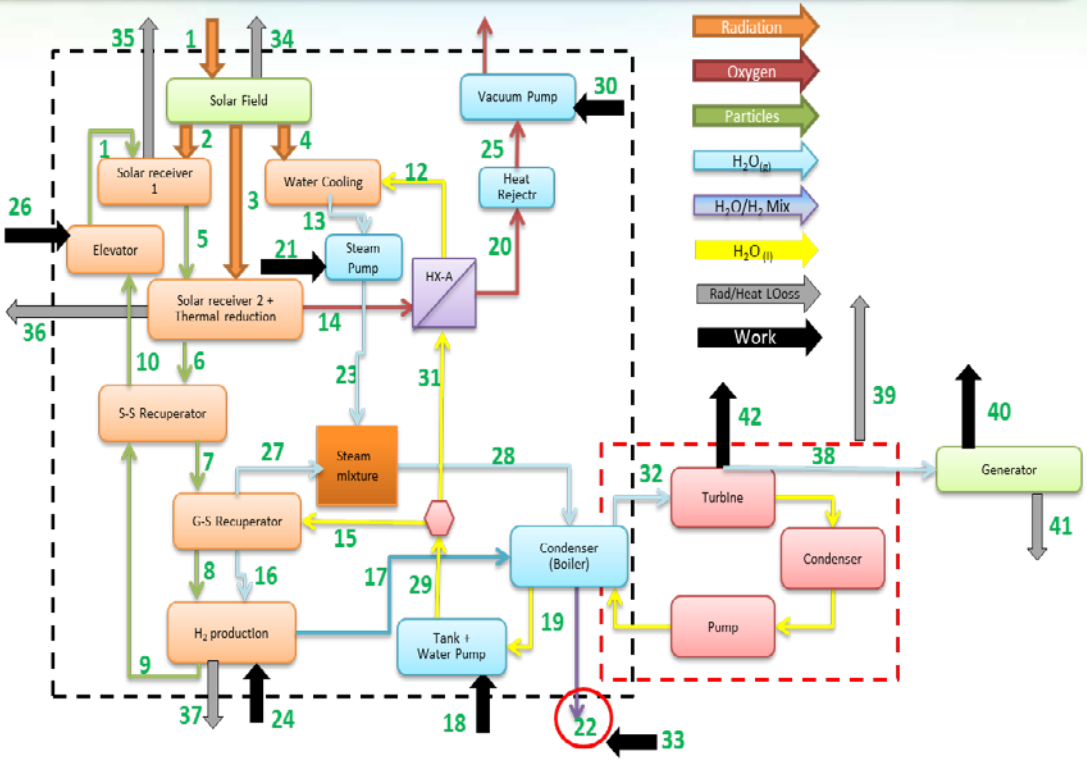


Technical Accomplishments and Progress: Completed Plant Predictor Model

Sensitivity and cost-performance tradeoff analysis now possible.

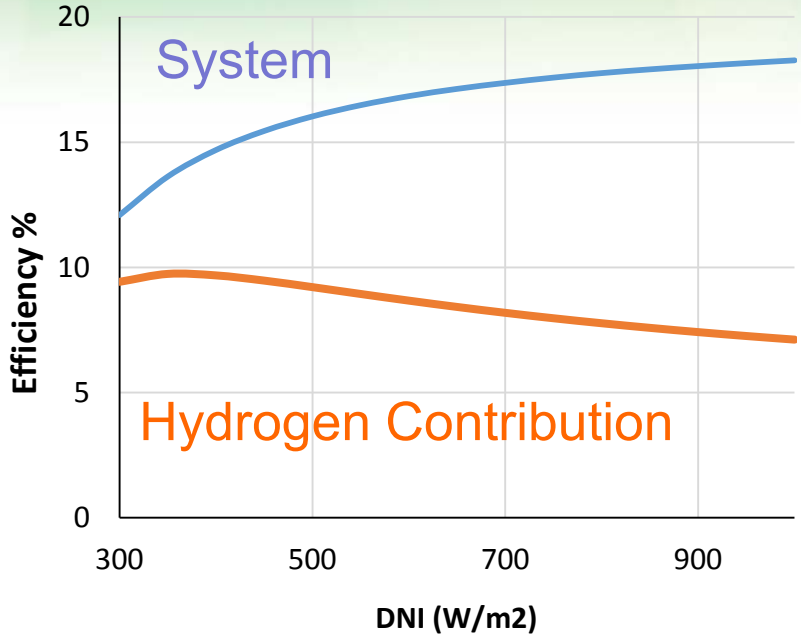
Features

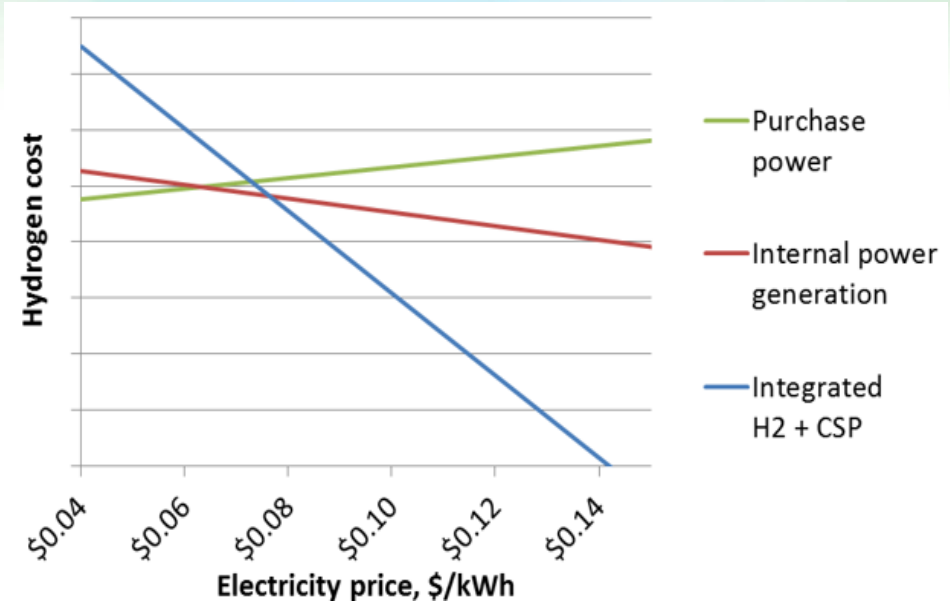
- Beam-up solar field design with CPC secondary concentrators
- Multiple receivers and multiple windows for particle reduction and pre-heating
- Heat exchange and recuperation
- Full mass/energy balance at each DNI
- Rankine cycle to produce electricity from the steam



- Detailed sub-models for 17 major components coupled using mass and energy balances between 42 streams.
- Quasi-steady state solution method that dynamically follows DNI.
- Operational and design parameters directly inform cost analysis.

Technical Accomplishments and Progress: Co-gen Electricity & H_2





- Electricity production from waste heat can offset H_2 cost.
  - Ratio of H_2:Electricity dependent on DNI
  - System efficiency is more complex
  - Impact of high-temperature waste heat amplified by integration with CSP

Cogeneration can achieve DOE H_2 cost targets even if solar-to-H_2 conversion efficiency for H_2 plant does not meet DOE targets.

Response to Previous Year Reviewer's Comments

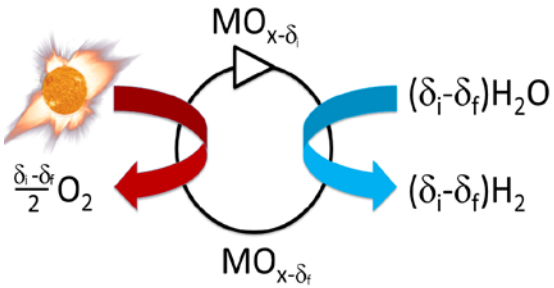
Comments are paraphrased and thematic.

FY16 Comments	FY17 Response
Technology is in its infancy, and while it has potential to make an impact, many technical challenges need to be solved before future impact can be assessed.	STCH is a low TRL, advanced approach to water splitting that promises to meet DOE cost targets. This project has made great strides to address both materials and reactor design challenges, and is currently poised to verify performance of Sandia's patented moving particle bed technology at small scale (3-5 kW_{th}). This will further inform our understanding of future impact.
The techno-economic analysis is important because it helps to identify the critical technical challenges, which might influence project strategy. It should have been an earlier objective in order to make a convincing case for achieving $2/kg hydrogen.	H2A was used for TEA early in the project to assess and address key technical challenges. Since then, our approach has produced a much higher fidelity full-system model, which has informed and advanced our thinking about plant design. For example, we have investigated the value of cogenerating H_2 and electricity and found synergies with CSP-electricity generation that have the potential to achieve $2/kg H_2 even at lower STH efficiency.
Has progress has been made in coordinating across research communities to establish conventions for analysis, best practices, and key measurements, and in coordinating and communicating materials discovery approaches, testing protocols, and reporting standards.	Yes, as a result of new DOE investments, the Hydrogen Advanced Water Splitting Materials Consortium has been established. This effort spans AE, PEC, and STCH technology pathways, and mandates the aforementioned activities.

Collaborations

Material Discovery and Characterization Team

- Colorado School of Mines, Golden CO.
  - Prof. Ryan O'Hayre, Prof. Michael Sanders, Ms. Debora Barcellos
  - Novel material formulations, synthesis, and screening
- Northwestern University, Evanston IL.
  - Prof. Christopher Wolverton, Mr. Antonie Emery
  - Application of quantum theory to engineering materials
- Stanford University, Stanford CA.
  - Prof. William Chueh, Dr. BG Gopal, Ms. Nadia Ahlborg
  - Entropy engineering of materials



Reactor Design, Testing, and Demonstration Team

- Bucknell University, Lewisburg PA.
  - Prof. Nathan Siegel
  - Particle heat transfer, solar simulator design, CPR2 assembly and testing
- German Aerospace Center-DLR , Cologne DE
  - Dr. Christian Sattler, Dr. Justin Lapp, Dr. Abisheck Singh, Dr. Stefan Brendelberger, Mr. Johannes Grobbel
  - Solar particle receiver design, fabrication, and testing

Systems Analysis Team

- Arizona State University, Tempe AZ.
  - Prof. Ellen Stechel, Prof. Nathan Johnson, Dr. Briana Lucero
  - Development of unit operations models, detailed large-scale plant design, technoeconomic analysis
- German Aerospace Center-DLR , Cologne DE
  - Dr. Martin Roeb
  - Detailed large-scale plant design, technoeconomic analysis

Remaining Challenges, Barriers, & Future Work

Challenges

- Discovering a redox material that will meet or exceed DOE cost and performance targets.
  - DOE's Hydrogen Advanced Water Splitting Materials Consortium (H2awsm.org) investments will focus on material discovery
- Establishing the CPR2 as a "routine-use" R&D tool to support H2awsm and attract commercial interest/investment.
  - Identified issues with particle flow control and thermal management that stymied efforts to achieve FOA GNG
  - Other technical issues will present themselves as we "learn by doing"

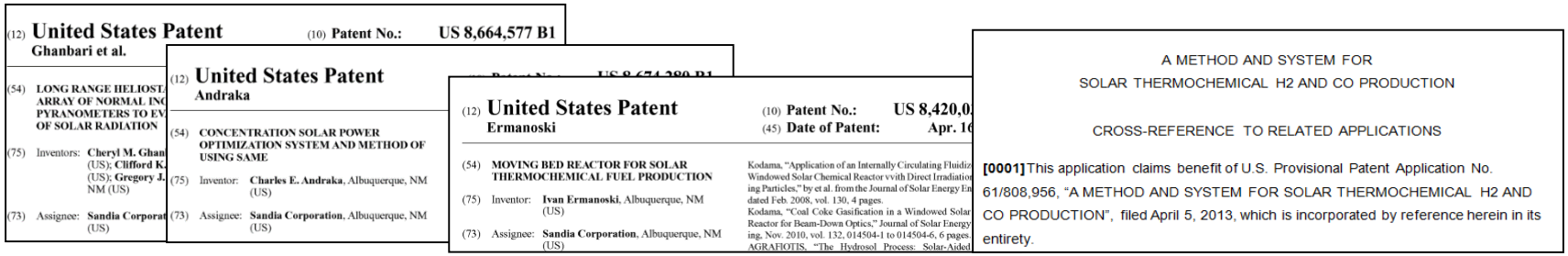
Future work*

- Upgrade CPR2 to increase reliability and provide service to H2aswm's customers.
  - Resolve known issues, rescale certain components for use with small material batches, and integrate second receiver-reactor and simulator to fully explore pressure cascade
- Publish project results in peer-reviewed journals.
  - 13 manuscripts in preparation on materials, reactor design, and TEA

*Project continuation and direction determined by DOE.

Technology Transfer Activities

- Sandia holds several patents on CSP, materials, and reactor technology.


(12) United States Patent
Ghanbari et al.
(10) Patent No.: US 8,664,577 B1

(54) LONG RANGE HELIOST ARRAY OF NORMAL INC PYRANOMETERS TO EV OF SOLAR RADIATION
(75) Inventors: Cheryl M. Ghan (US); Clifford K. (US); Gregory J. NM (US)
(73) Assignee: Sandia Corporat (US)

(12) United States Patent
Andraka

(54) CONCENTRATION SOLAR POWER OPTIMIZATION SYSTEM AND METHOD OF USING SAME
(75) Inventor: Charles E. Andraka, Albuquerque, NM (US)
(73) Assignee: Sandia Corporation, Albuquerque, NM (US)

(12) United States Patent
Ermanoski
(10) Patent No.: US 8,420,0
(45) Date of Patent: Apr. 16

(54) MOVING BED REACTOR FOR SOLAR THERMOCHEMICAL FUEL PRODUCTION
(75) Inventor: Ivan Ermanoski, Albuquerque, NM (US)
(73) Assignee: Sandia Corporation, Albuquerque, NM (US)

Kodama, "Application of an Internally Circulating Fluidiz Windowed Solar Chemical Reactor vvith Direct Irradiation ing Particles," by et al. from the Journal of Solar Energy En dated Feb. 2008, vol. 130, 4 pages.
Kodama, "Coal Coke Gasification in a Windowed Solar Reactor for Beam-Down Optics," Journal of Solar Energy ing, Nov. 2010, vol. 132, 014504-1 to 014504-6, 6 pages.
AGRAFIOTIS, "The Hydrosol Process: Solar-Aided

A METHOD AND SYSTEM FOR
SOLAR THERMOCHEMICAL H2 AND CO PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application No. 61/808,956, "A METHOD AND SYSTEM FOR SOLAR THERMOCHEMICAL H2 AND CO PRODUCTION", filed April 5, 2013, which is incorporated by reference herein in its entirety.

- Operating the CPR2 is paramount to technology transfer plan in order to attract and develop industry relations.
  - Roadmap based on demonstration, advancing TRL, and economic analysis
  - Need to present value-added propositions to industrial gas suppliers & CSP electricity providers
- Leverage relationship with DLR to promote international interest in technology development.

Summary

- Developed new knowledge about (AE, RE)Mn-based redox active perovskites that is gradually leading towards material design rules.
- Completed construction and shakedown tests of CPR2.
  - Reactor fully operational
  - Poised to meet FOA requirement making 3L H_2 in <<8 hours
- Demonstrated a clear path towards commercialization that leverages the value of H_2 and electricity cogeneration.
  - STC-H_2 is the only renewable hydrogen production technology that generates and can export high-quality waste heat

Accomplishments represent significant progress towards overcoming technical barriers to STCH development.

Thank You.

Questions?

Technical Back-Up Slides

System Components in TEA and Performance Modeling

- Solar Field – Focuses solar radiation to multiple windows and multiple cavity receivers
- Tower – Contains receiver, reactor, and supporting components
- Receiver 1 – Used to pre-heat particles (three windows and three CPCs)
- Elevator – Moves particles up to the tower
- Receiver 2 – Used to reduce particles (multiple windows, multiple receivers, CPCs that cascade to the final reduction pressure while removing oxygen from particles)
- Solid-Solid Recuperator – Exchanges heat between particles going moving upward to (re-oxidized) and downward from (reduced)
- G-S Recuperator – Cools reduced particles to the re-oxidation temperature and generates steam for water splitting and electricity
- Fuel Production Chamber – Mixes reduced particles with steam to generate H_2
- Heat Exchanger A – Cools oxygen exiting solar receivers
- Steam Mixture – Mixes steam from G-S Recuperator and water to cool receiver components
- Heat Rejecter – Cools oxygen to room temperature (to improve pump performance)
- Vacuum Pump – Pumps oxygen out of the receivers
- Steam Pump – Pumps steam through the system
- Condenser – Separates H_2 from steam and rejects heat for use in a power cycle
- Rankine Cycle – Power cycle used to convert heat energy into mechanical power
- Water Tank with Pump – Water storage and supply
- Generator – Produces electrical power from mechanical power in Rankine Cycle

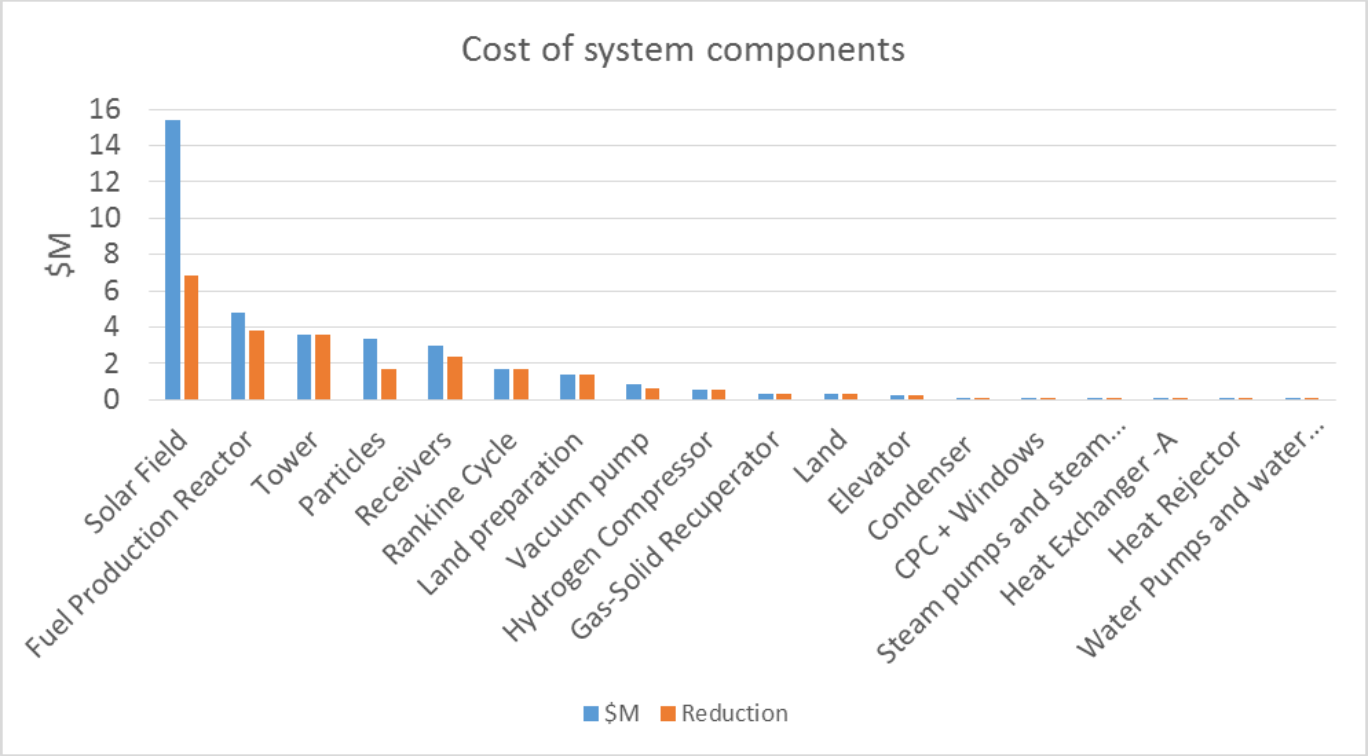
Detailed Cost Estimation

- Increased fidelity of CAPEX estimation.
- Includes scaling relations that are not strictly linear with size.
- Initial cost estimate $9.86/kg H_2.
  - Assumes $60/MWH revenue for electricity
  - $170/m^2 Heliostats
  - 11%/year CAPEX charge
  - $3.2 B (exports electricity) vs original estimate of $1.5B (+ purchased electricity)

- Realistic cost reductions for Ultimate Case.
  - Increased H_2 per tower, decreased electricity production, and reduced revenue per electrical unit
  - $75/m^2 Heliostats
  - Decreased cost of particles, increased lifetime
  - Modest cost reduction of receivers and vacuum pumps
  - More favorable cost of money 8%/yr
  - Ultimate estimate **$2.11/kg H_2**

Component	$M	Reduction	% change
Solar Field	15.429	6.807	44.1%
Land	0.349	0.349	
Land preparation	1.414	1.414	
Tower	3.606	3.606	
Receivers	2.981	2.385	80.0%
CPC + Windows	0.132	0.132	
Elevator	0.227	0.227	
Particles	3.356	1.678	50.0%
Fuel Production Reactor	4.777	3.822	80.0%
Water Pumps and water system	0.025	0.025	
Steam pumps and steam system	0.074	0.074	
Heat Exchanger -A	0.041	0.041	
Gas-Solid Recuperator	0.367	0.367	
Condenser	0.134	0.134	
Heat Rejector	0.027	0.027	
Vacuum pump	0.896	0.672	75.0%
Hydrogen Compressor	0.538	0.538	
Rankine Cycle	1.714	1.714	
Total per tower	36.087	24.011	66.5%
All Towers	2959.147	1310.079	75.0%
Controls	147.957	65.504	44.3%
Balance of Plant	88.774	39.302	44.3%
Total CAPEX including Installation	3195.879	1414.885	44.3%
Contingency+Indirect	1105.774	489.550	44.3%
Total Fixed Cost	4301.653	1904.435	44.3%
Annual capital charge	473.182	152.355	72.7%
Particle Replacement	0.671	0.168	50.0%
Total Variable Cost	1.910	1.528	80.0%
Total Annual Cost	475.763	154.051	32.4%
Average Production per Tower	447.56	671.33	150.0%
Total Production	100.55	150.82	150.0%
Revenue Hydrogen	361.683	116.024	21.4%
Average Net Electrical per Tower	23.19	11.59	50.0%
Total Production	5.21	2.60	50.0%
Revenue Electricity	114.080	38.027	66.7%
Unit hydrogen	**9.860**	**2.110**	

CAPEX Dominates Cost



- Biggest cost reduction opportunity per tower is the solar field.
- Next biggest opportunity comes from productivity, i.e., fewer towers.