

Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

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Sandia National Laboratories

DOE Annual Merit Review
16.05.2013

Project ID: PD081

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Timeline

- Project Start Date: 10/2008
- Project End Date: 10/01/2013*
- Project Complete: TBD

Budget

- Total project funding to date.
DOE share: \$4737K (2008-2013)
Contractor share: \$608K
- Funding for FY13.
\$435K (SNL)
- Planned Funding for FY14.
\$500K (SNL)

Barriers Addressed

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

Partners

- Bucknell University, Lewisburg PA.
Prof. Nathan Siegel
- Colorado School of Mines, Golden CO.
Prof. Jianhua Tong
- University of Colorado, Boulder CO.
Prof. Alan Weimer

*Project continuation and direction determined annually by DOE.

• **DOE Objective:** By 2015, 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.

- **Project Objective:** Develop a high-temperature solar-thermochemical reactor and redox materials for *efficient* hydrogen production based on a two-step, non-volatile metal oxide cycle.
- **2012-2013 Objectives:**
 - Design particle receiver-reactor concepts and assess feasibility.
 - Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical cycles.
 - Construct and test reactor prototypes.

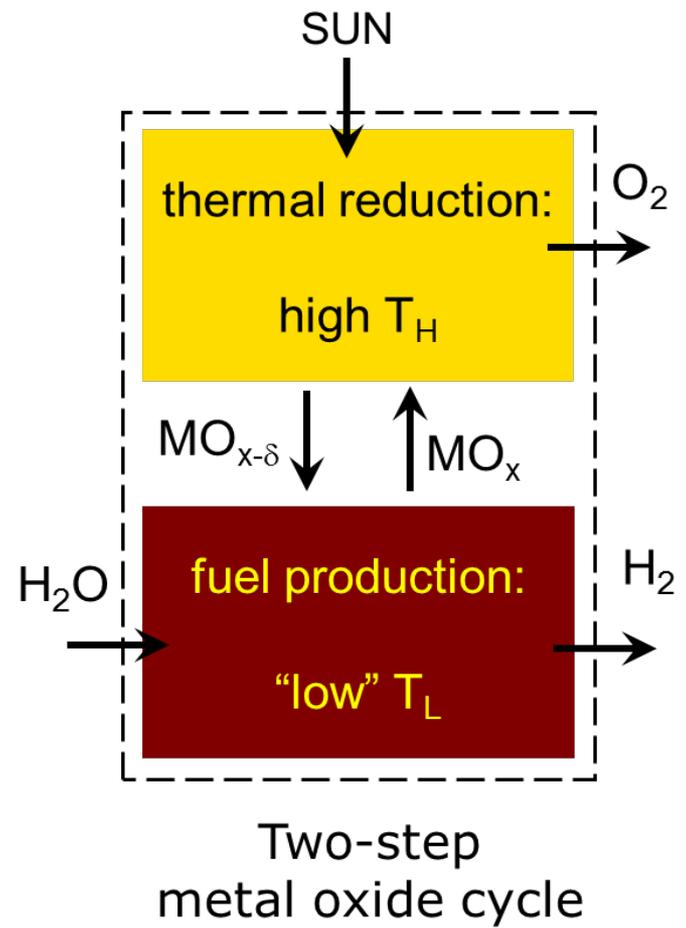
Technical Efforts Target Three Key Areas

- Systems analysis.
 - Refine estimates for H₂ production cost
- Materials discovery and characterization.
 - Target perovskite oxides exclusively

property	ceria (CeO ₂)	perovskite (ABO ₃)	ideal
redox kinetics	FAST	TBD	FAST
redox capacity	LOW	HIGH	HIGH
reduction T _H	HIGH	LOW	LOW
durability	HIGH	TBD	HIGH
earth abundance	LOW/MED	HIGH	HIGH

- Assess 3 critical material functions:
 - O₂ uptake-and-release
 - onset temperature for thermal reduction
 - oxidation kinetics

- Reactor design and development.
 - Particle reactor with novel beam-down optics
 - Reactor design and material are critically linked



• Reactor efficiency is the biggest cost driver.

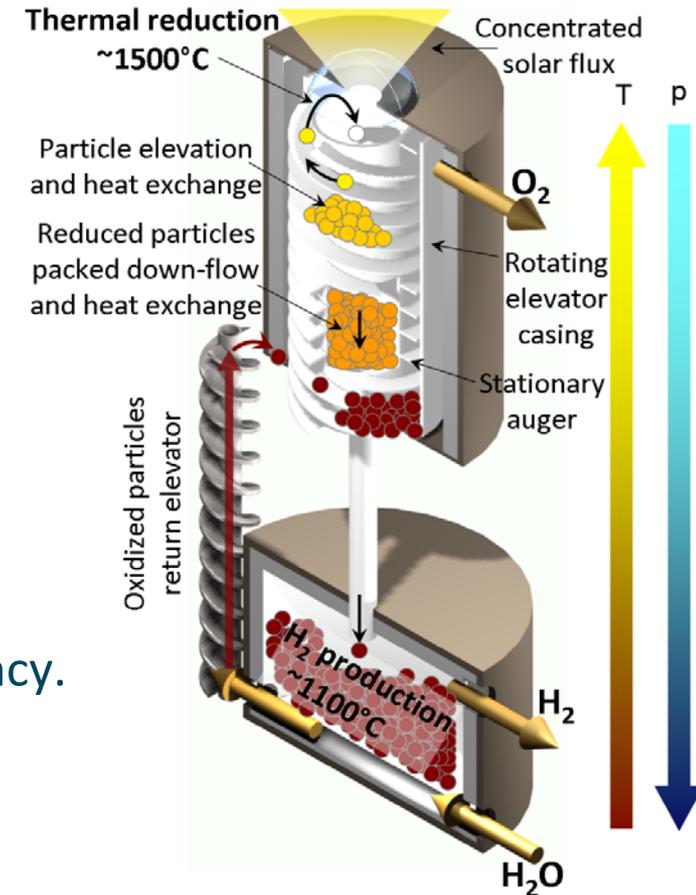
Milestones and Progress

03.2012-03.2013 Accomplishments

ACTIVITY	MILESTONE	COMPLETE
Assess hydrogen production cost from a particle reactor using the H2A3 tool	analyzed 100,000 kg H ₂ /day parabolic-dish based facility using CeO ₂ , sensitivity analysis reveals reactor efficiency is the biggest cost driver	80%
Develop design principles for perovskite modification.	formulated three methods based on thermodynamics (ΔH , ΔS , $[V_o^{**}]$) and perovskite structure theory	30%
Synthesize a small number of candidate redox materials.	sol-gel and solid state reactive sintering used to synthesize 45 perovskite and 5 ceria compounds	100%
Characterize the thermodynamic and kinetic performance of new materials.	new materials screened using TGA protocol, conducted detailed kinetic studies on 6 materials	50%
Discover new redox active perovskites.	Sr _{1-x} La _x Mn _{1-y} Al _y O ₃ has ~3× greater redox capacity than CeO ₂ at 150 °C lower T _{reduction} , patent filed	20%
Theoretically analyze Sandia particle reactor performance	demonstrated that reactor operates near peak solar-to-H ₂ efficiency on an annual average, also can produce excess electricity AND water from waste heat	100%
Design and test particle reactor concepts	constructed testing platform, measured >30 g/s particle conveyance on recuperating auger prototype, found bed permeability is low enough for pressure seal	60%
Develop system-level designs and analyses of a central-receiver based platform.	designed novel beam-down optics for 3 MW tower, assessed thermal management of secondary reflector	50%

Reactor Efficiency Drives R&D

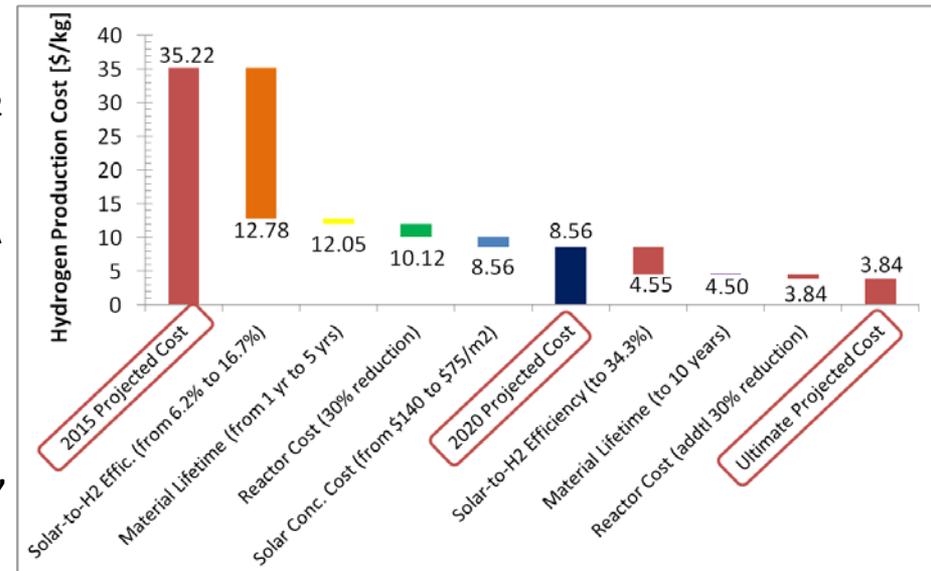
- Moving material to sun increases efficiency.
 - Particle transport necessary for continuous operation
- Temperature cycling increases efficiency.
 - Solid-solid heat exchange necessary for recuperation
- Reducing under vacuum increases efficiency.
 - Particle bed necessary for pressure separation
- High redox capacity material increases efficiency.
 - Bulk materials with low reduction enthalpy necessary for deep cycling



- **Incorporating ALL design attributes make it possible to achieve DOE ultimate cost target for H₂ production.**

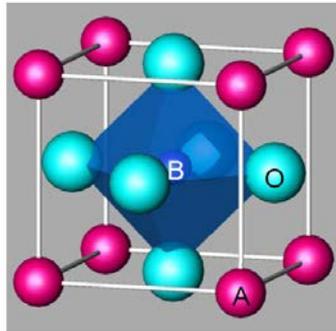
H2A3 Analysis of 100,000 kg H₂/day Plant

- Sandia dish-based particle reactor.
 - CeO₂ active material:
variable solar efficiency
 - 22,155 parabolic dishes over 13 km²
 - 88 m² per dish
 - Meteorological data for Daggett, CA
 - Centralized delivery at 300 psia H₂
- 380 MW_{TH}.
 - Main electrical loads are dish drives, H₂ pumping, and H₂O pumping provide by solar
- Analysis conducted in collaboration with Strategic Analysis, Inc.



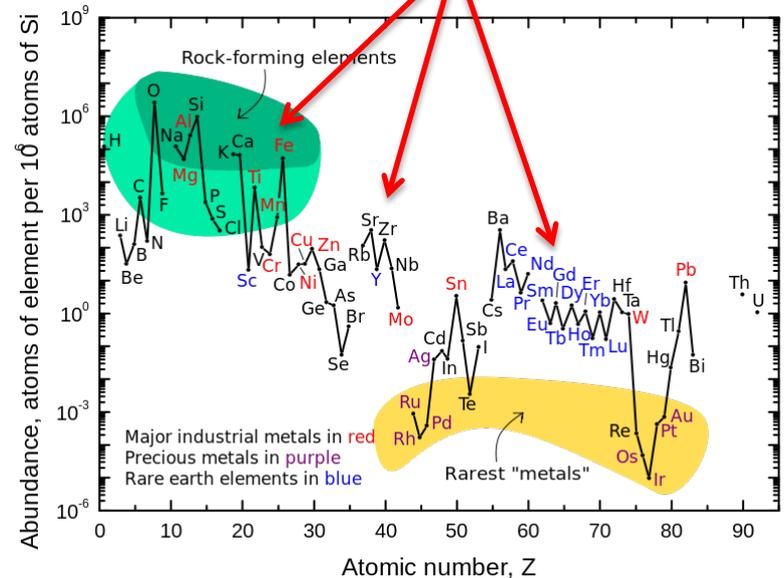
- Increased reactor efficiency yields significant reduction in H₂ costs.
- Reactor design and materials are critically important.

Material Discovery Effort Focused on Perovskites



- Synthesized 45 compounds from 9 elements.
 - Al, Cr, Ce, Fe, La, O, Sr, Ti, Zr
 - Sol-gel or Solid State Reactive Sintering
- Identified promising candidates using TGA screening.
- Detailed kinetic measurements on 6 materials in Sandia's laser-heated stagnation flow reactor.

perovskites fall in these regions

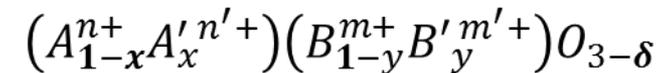
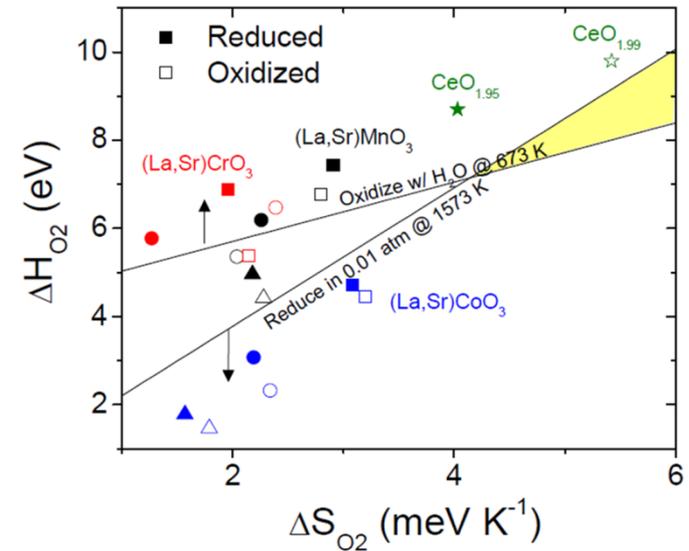


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• More ideal materials increase solar-to-hydrogen efficiency.

Design Principles for Perovskite Modification

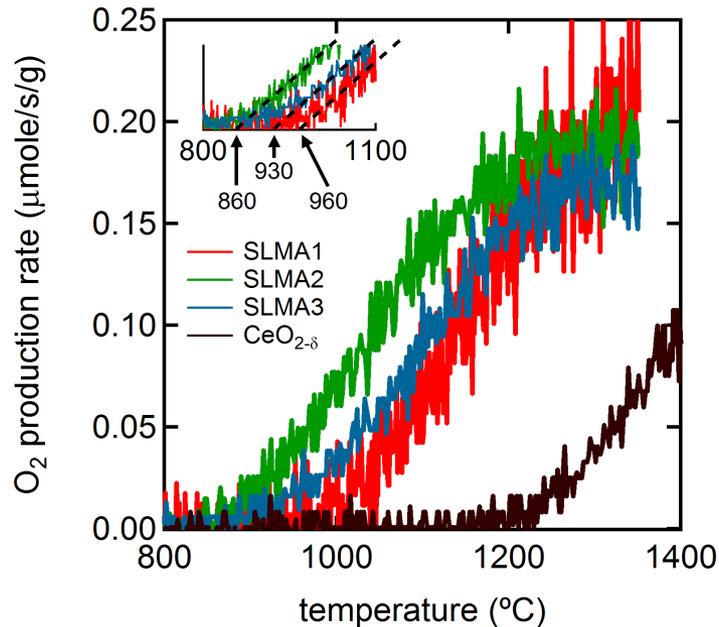
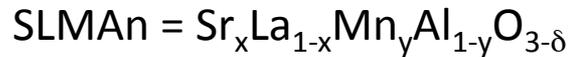
- Method 1: reduction enthalpy and entropy.
 - Taken from published data
- Method 2: oxygen non-stoichiometry.
 - Taken from published data
- Method 3: perovskite structure theory.
 - Goldschmidt tolerance factor
ionic radii ($r_{A'}$, r_B , r_O)
 - Redox active B-site transition metal
 - Heterosize A-site substitution ($r_{A'} \neq r_A$)
 - Heterovalent A-site substitution ($n'_{A'} \neq n_A$)



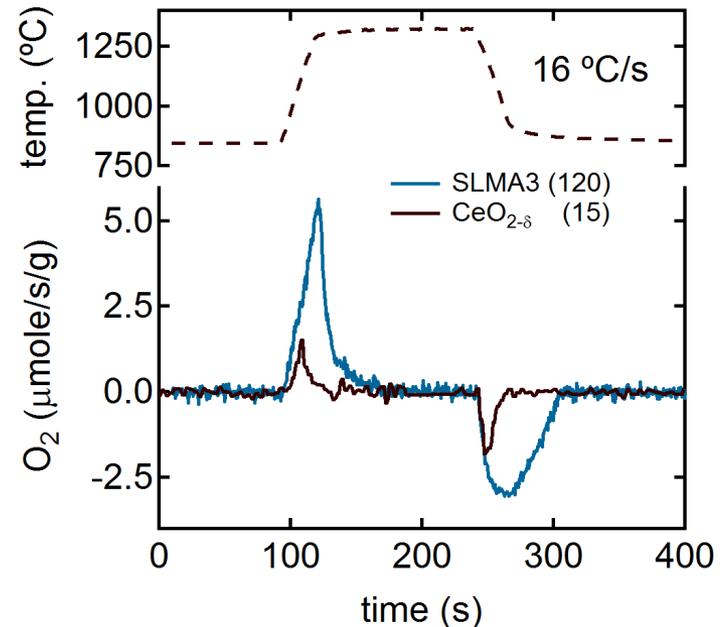
$$(r_A + r_O) / \sqrt{2}(r_B + r_O) \sim 1$$

- Large oxygen non-stoichiometry ($ABO_{3-\delta}$, $0.5 \geq \delta \geq 0.1$) = high capacity.
- High oxygen mobility = fast kinetics.

Discovered Perovskite with Lower Reduction Enthalpy than CeO_2

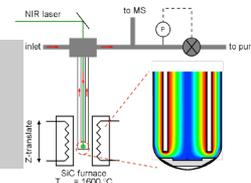


- Onset of O_2 evolution 300°C lower than CeO_2 .



- Perovskite oxygen yield $8 \times >$ CeO_2 at $T_R = 1350^\circ\text{C}$.
- $\delta_{\text{PEROVSKITE}} \gg \delta_{\text{CERIA}}$

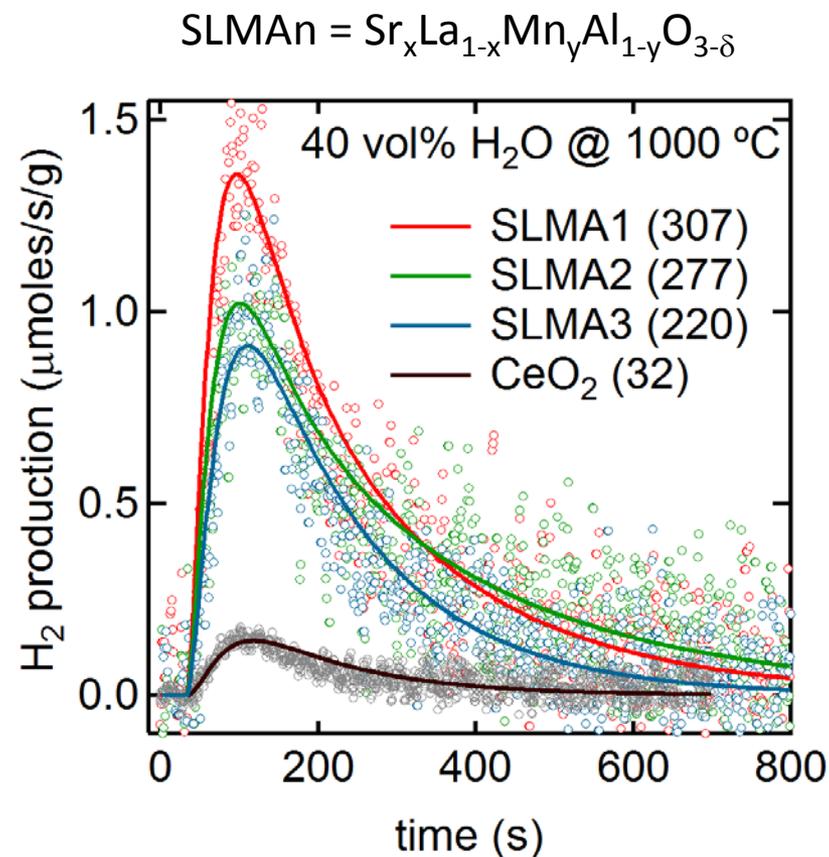
- Lower reduction temperature and larger non-stoichiometry (δ) increase solar-to-hydrogen efficiency.**



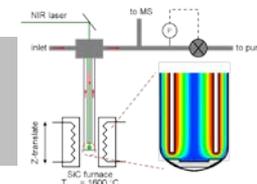
Discovered Perovskite with Higher Capacity at lower T_R than CeO_2

- Perovskite compounds split H_2O in a thermochemical cycle.
 - First of a kind observation
- Kinetics benchmarked against CeO_2 .
 - Similarly fast oxidation rates
- Make $\sim 9\times$ more H_2 than CeO_2 at $T_R = 1350\text{ }^\circ\text{C}$.

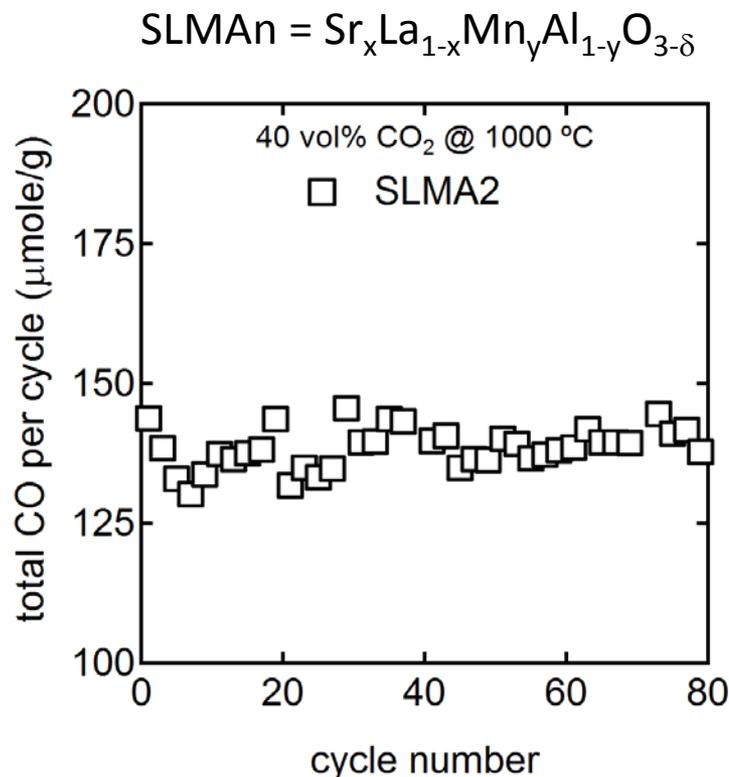
compound	H_2 ($\mu\text{mole/g}$)
SLMA1	307
SLMA2	277
SLMA3	220
$CeO_{2-\delta}$	32



- Patent filed on a family of Sr- and Mn- substituted $LaAlO_3$.**
- Likely many other perovskites that can perform even better!**

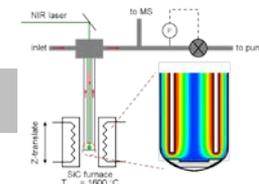


Perovskite Materials are Durable



- Conducted 80, 30 minute CO₂ splitting cycles.
- 15 min reduction at 1350 °C, 15 min oxidation at 1000 °C.
 - Heating rate = 6 °C/s

• No short-term degradation mechanisms visible in perovskite.



Theoretical Analysis of Sandia Reactor Concept: Solar-to-H₂ Efficiency

$$\eta = \left(\frac{P_{TH}}{P_S} \right) \left(\frac{HHV_{H_2}}{Q} \right) = \frac{\dot{n}_{H_2} HHV_{H_2}}{P_S} \rightarrow \dot{n}_{H_2} = \frac{P_{TH}}{Q}$$

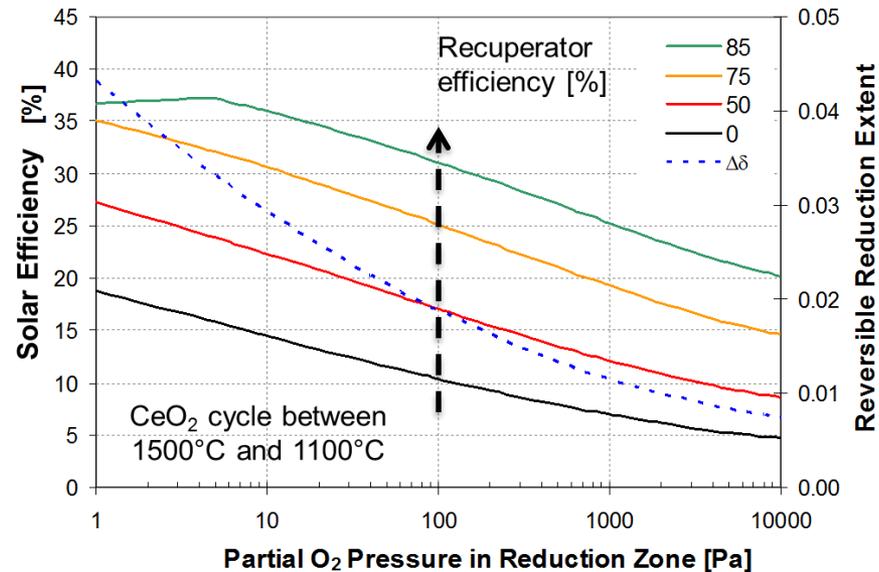
$$P_{TH} = r_{12} * r_d * t_W * A * P_S - P_{rad}$$

$$Q = Q_{TR} + Q_{SH} + Q_{AUX}$$

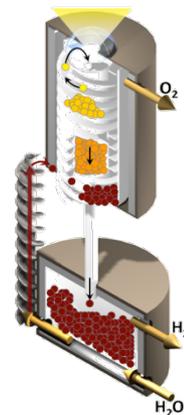
new materials impact Q and P_{TH}

All-inclusive efficiency metric:

- Collection losses.
 - Concentrator and re-radiation
- Oxide heating.
- Oxide thermal reduction.
- Feedstock heating (steam).
- Pumping.
- Electrical/mechanical work.

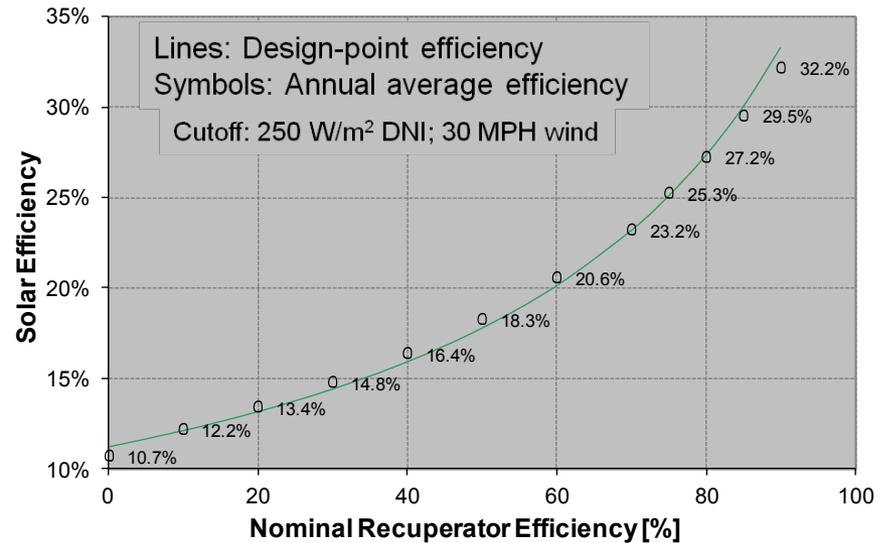
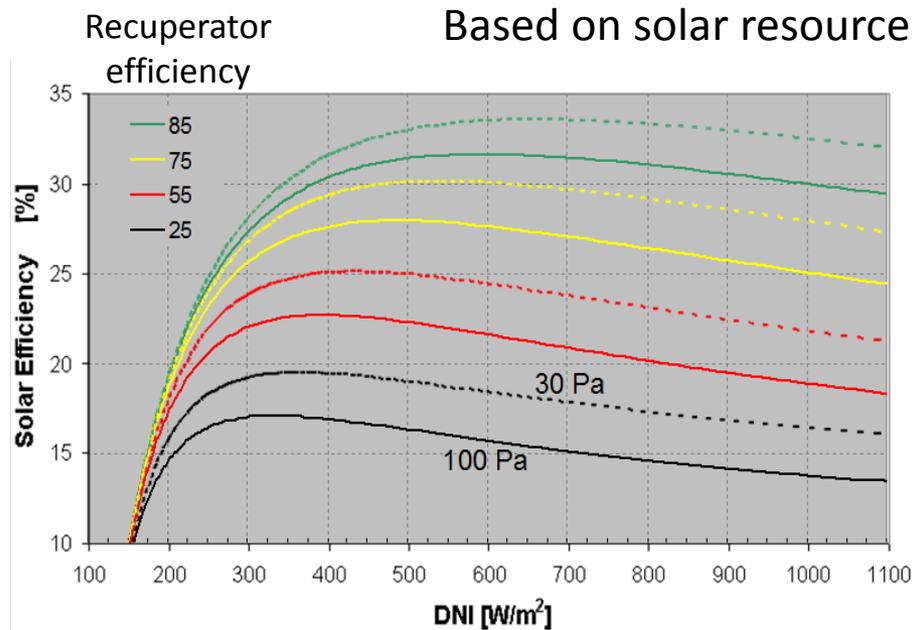


increased efficiency at larger $\Delta\delta$



- **Solar Efficiency = Solar-to-H₂ conversion efficiency based on HHV.**
- **Model is used to explore optimal reactor operating conditions.**
- **Model is used to assess performance gains from new materials.**

Annual Average Solar Efficiency \approx Peak Efficiency



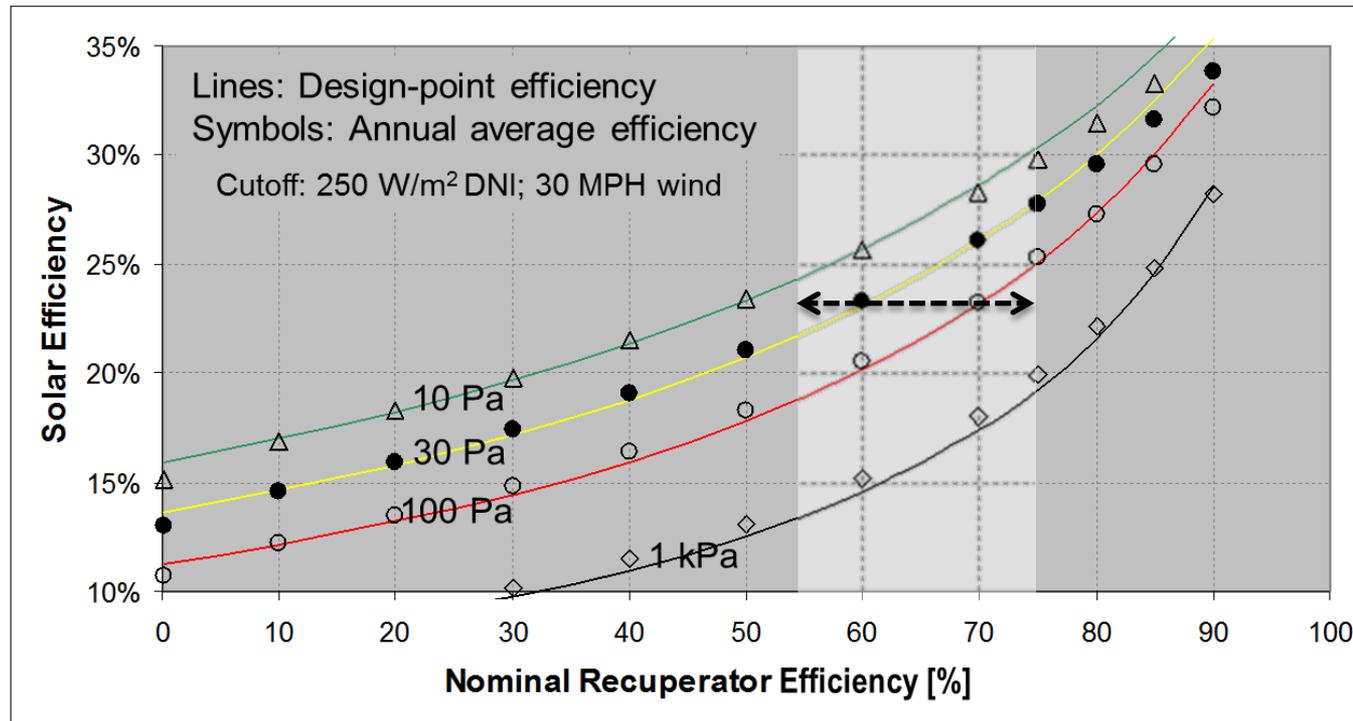
- Solar efficiency weakly dependent on DNI in particle reactor.
 - Change particle flow rate to maintain design point efficiency

- Annual average efficiency nearly equal to design point efficiency.
 - Weak DNI dependence

- **Reactor ALWAYS operates near peak efficiency.**
- **Compensate for solar variability ($400 < \text{DNI} < 1000$).**



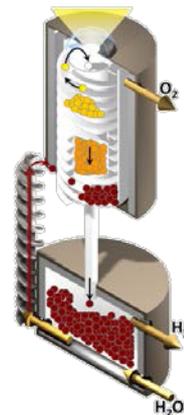
Annual Average Efficiency Dependent on O₂ Pressure



increased efficiency at lower O₂ pressure

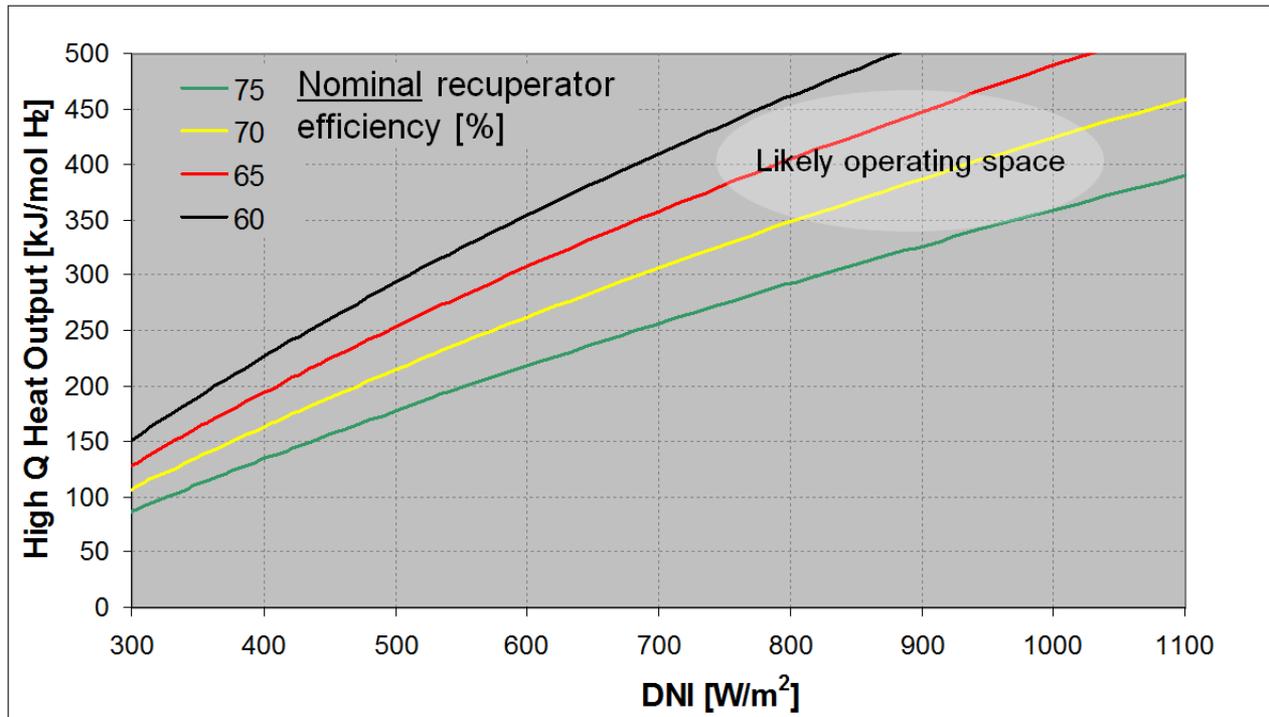
- Pumping speed and recuperator efficiency affect solar efficiency.
- Increase solar efficiency by lowering O₂ pressure and raising recuperator efficiency.

- **Pumping speed can compensate for poor heat recuperation.**
- **Vice Versa.**



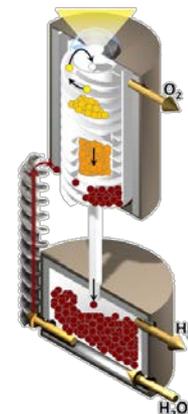
Produce H₂O and Excess Electricity

Water condensation: ~ 3 kJ/mol (0.85 kJ/mol theoretical)

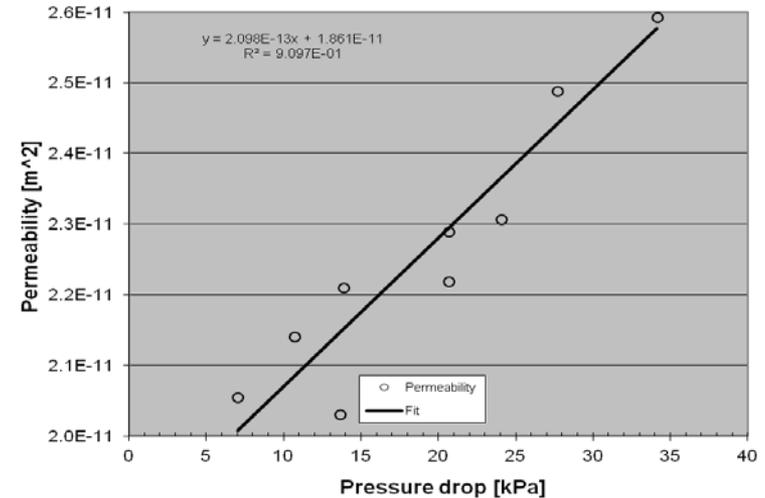
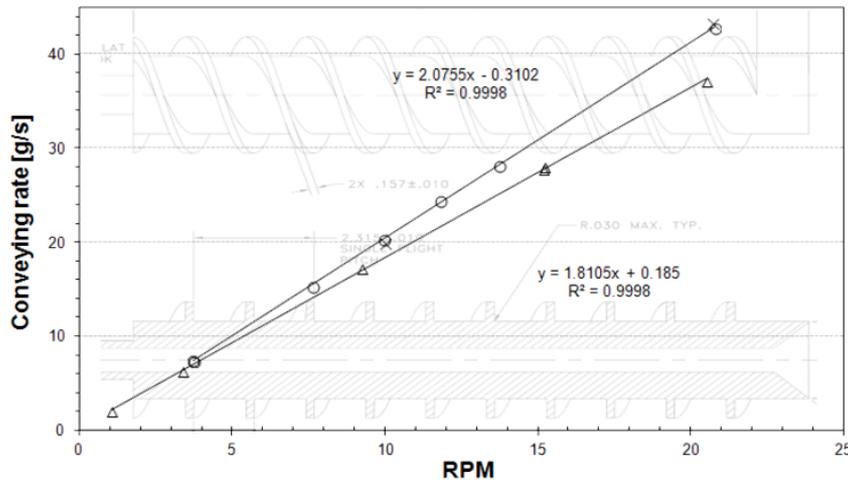


- High quality waste heat can generate electricity and produce water.
 - Use absorption chiller to condense water from the atmosphere
 - Sell excess electricity

• Year-round operation using only sunshine and air.
• No need to find or pipe H₂O into desert.



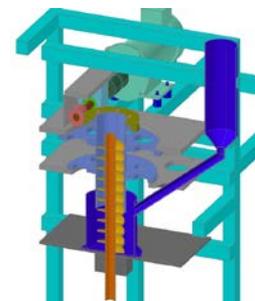
Prototype Validates Conveyance and Pressure Separation



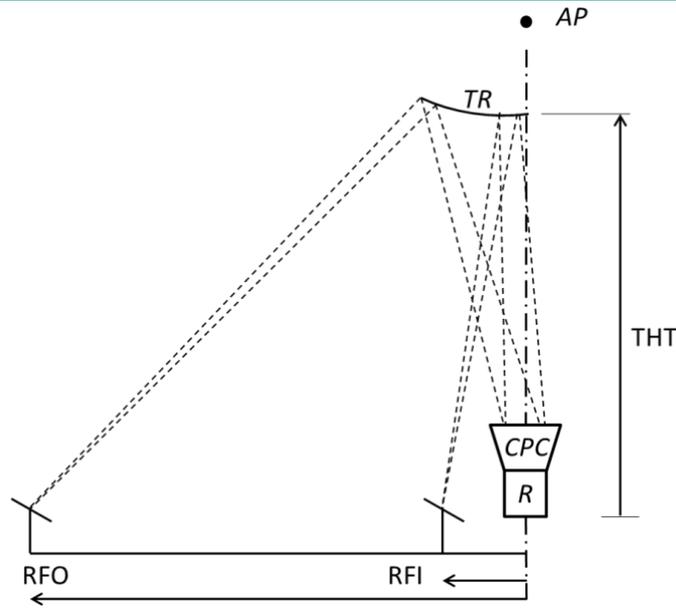
- Conveying rate far exceeds particle flow requirement.
 - Tested prototype auger designed for heat recuperation
 - Narrow fined, double helix

- Bed permeability sufficient for sealing.
 - Pressure separation key to high efficiency

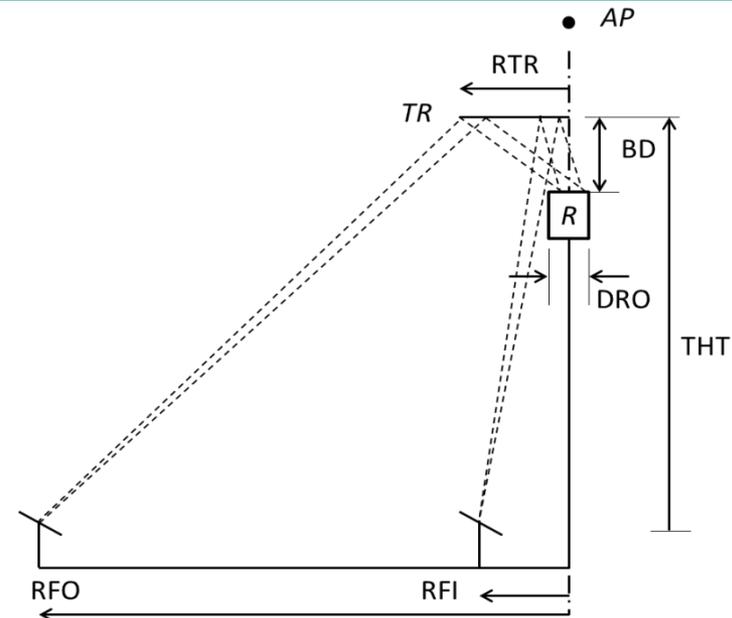
• **No technical show stoppers!**
 • **A clear path to high temperature prototype development.**



Particle Reactor Requires Beam Down Optics



Conventional Beam Down Tower

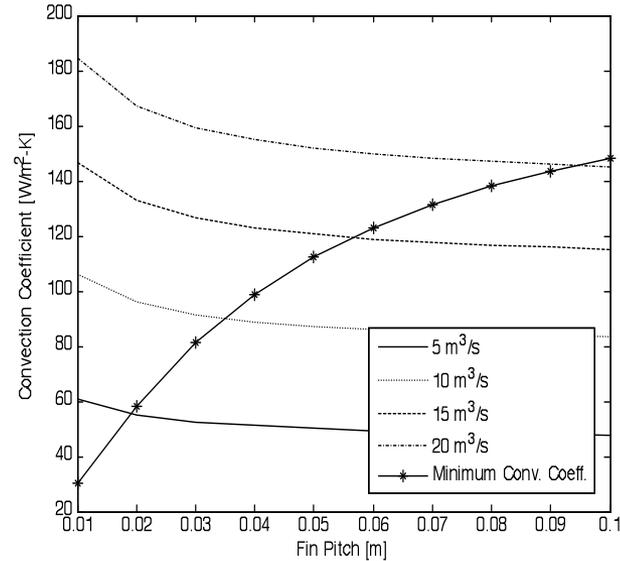
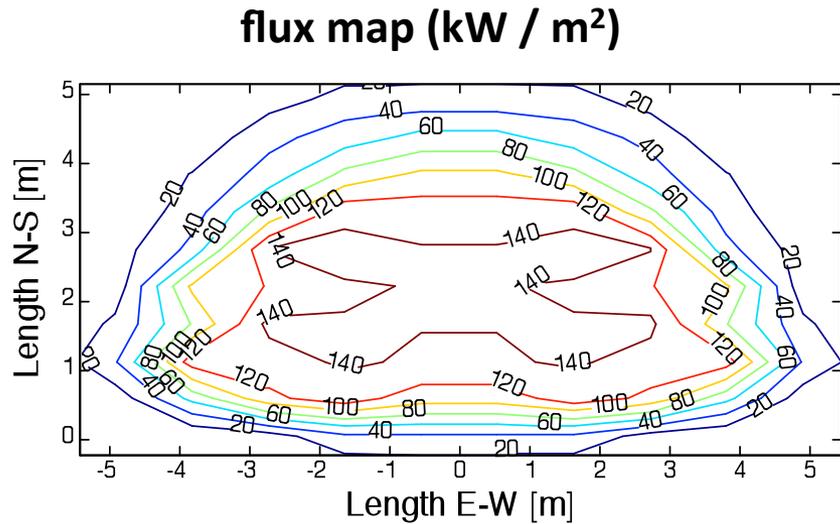


Modified Beam Down Tower

- 3 MW_{TH} , 75 m tower height, 6606 heliostats (1 m^2 mirror).
 - Reactor located near tower reflector
 - $1,600 \text{ kW/m}^2$ on 2 m aperture, peak flux $> 6,000 \text{ kW/m}^2$
 - Terminal concentrator not needed
- Flat tower reflector must tolerate high solar flux $\sim 140 \text{ kW/m}^2$ (140 suns).

• **Basis for a central receiver H2A3 analysis.**

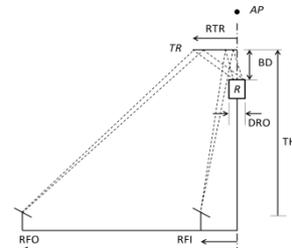
Assess Thermal Management of Reflector



$$h_{\min} = \frac{\alpha * \text{Flux}}{(T_{\text{surface}} - T_{\text{air}}) \left(\frac{2H_{\text{fin}}\eta_{\text{fin}}}{\text{Pitch}} + 1 \right)}$$

- Evaluating forced air convection for thermal management.
- Back surface mirror provides durability needed for outdoor operation.
 - 5-10% of incident solar energy absorbed by the mirror
- Max allowable mirror temperature between 100-160 °C.

• Cooling secondary mirror not an issue.



- Prof. Nathan Siegel at Bucknell University.
 - Solar interface, systems and economic analysis
- Prof. Jianhua Tong at the Colorado School of Mines.
 - Perovskite synthesis and TGA screening
- Prof. Alan Weimer at the University of Colorado.
 - Students in residence at SNL/CA characterizing Sandia materials

- Estimated FY14 funding target.
 - Continue perovskite research and development. Use lessons learned from early success to propose and validate composition—activity relationships. Investigate ABO_3 formulations from earth-abundant elements (rock-forming elements).
 - Modify engineering test stand for high-temperature operation ($< 5 \text{ kW}_{\text{TH}}$ operating off-sun). Evaluate designs for solid-solid heat exchange, oxidation chamber, particle conveyance, gas flow, durability, etc. Investigate tradeoffs between recuperation, pumping, and material activity. Validate and refine reactor model.
 - Complete H2A3 analysis for our centralized receiver design. Include sensitivity studies to resolve critical paths for reducing H_2 production costs.
 - Evaluate optical components for the beam-down design using Bucknell University's Solar Simulator.
- Funds in modest excess of FY14 estimate.
 - Upgrade stagnation flow reactor to operate at higher pressure (1-2 atm) and higher throughput. Minimize material characterization bottleneck.
 - Initiate computational material screening effort using DFT methods.
 - Build balance of plant infrastructure for engineering test stand to interface with Sandia's solar furnace (on-sun testing).

- Analyzed H₂ production costs for a parabolic-dish based particle reactor.
 - 100,000 kg H₂/day, DOE's ultimate cost targets are achievable
 - Sensitivity analysis reveals the importance of reactor efficiency
- Discovered Sr_{1-x}La_xMn_{1-y}Al_yO₃ perovskite that outperforms CeO₂.
 - Developed methodology for perovskite modification and material discovery
 - Synthesized and screened 45 compounds
 - Perovskite produces 9× more H₂ than CeO₂ at 150 °C lower reduction temperature
- Analyzed efficiency of Sandia particle reactor under various operating conditions.
 - Reactor ALWAYS operates at near peak solar-to-hydrogen efficiency
 - Reactor produces high quality waste heat to make excess electricity and provide water
- Validated particle conveyance and pressure separation in cold prototype.
 - Exceeded required particle flow rates (> 30 g/s)
 - Particle bed gas permeability sufficiently small to ensure vacuum-tight seal
- Designed beam-down optical system for particle reactor operating at 3 MW_{TH}.
 - Novel design for flat tower reflector
 - Heat management of tower reflector can be accomplished through air cooling

• **FY13 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.**

Technical Back-Up Slides

System Level: Many Losses and High Annual Efficiency

Resource efficiency = 95% for Daggett, CA (DNI > 300W/m²)

Operational ~ 94%

Equip. Availability = 97%, Blocking&Shading = 98%, Wind Outage = 99%

Optical ~ 79%

Reflectivity = 93% (two reflections)

Dirt = 95%

Window = 95%

Tracking = 99%

Intercept = 95%

Receiver ~ 82%

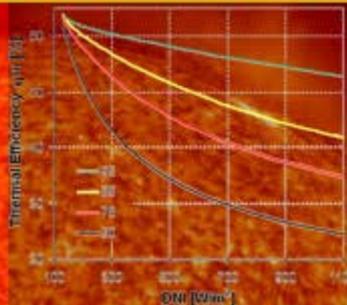
Radiation = 82%

Conduction/Convection = 0 %

Solar-to
heat:
~58%



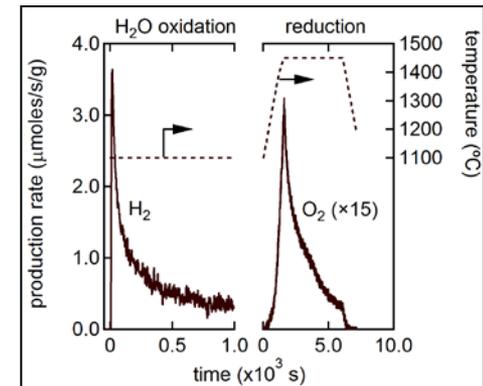
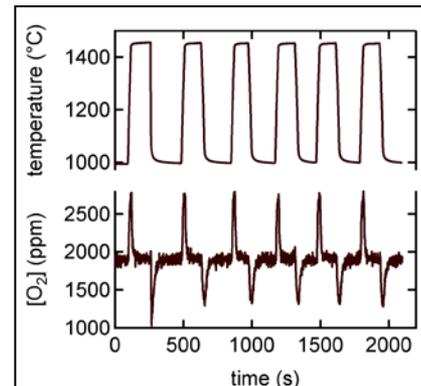
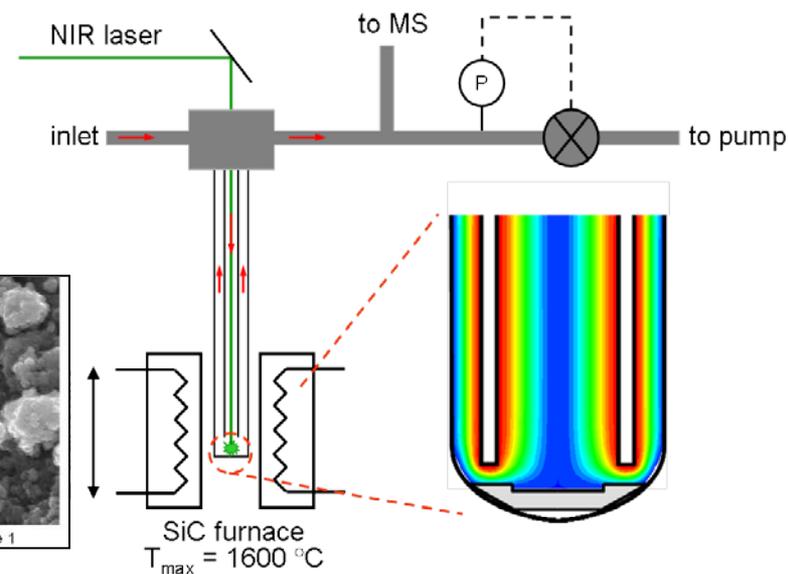
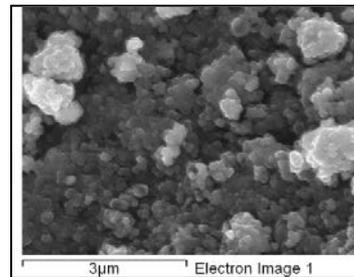
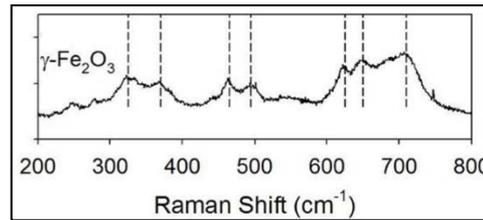
Thermal
~44%



**~25% solar to H₂
annual average**

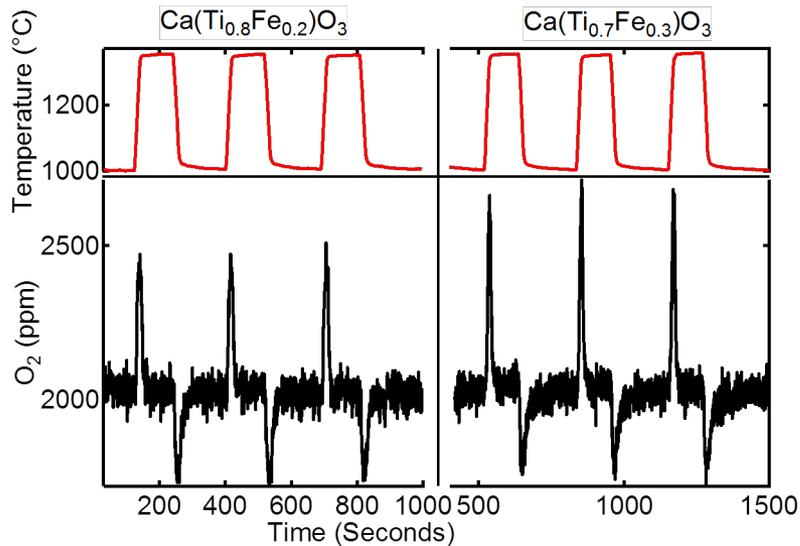
Experimental Methods for Characterizing Redox Materials

- Surface analysis.
 - Surface Raman, XPS
- Material properties.
 - BET surface area
 - SEM-EDX, TEM-EELS, XRD
- Kinetic measurements.
 - Stagnation flow reactor
 - 500 W CW NIR laser heating
 - Modulated beam mass spectrometer
- Screen for O₂ uptake and release.
 - Assess redox viability
- Resolve thermal reduction behavior.
- Resolve water splitting behavior.
 - Variable T, P, [H₂O]
- Analysis.
 - Resolve rate limiting mechanisms
 - Develop kinetic models
 - Evaluate material stability
 - Test cycle performance

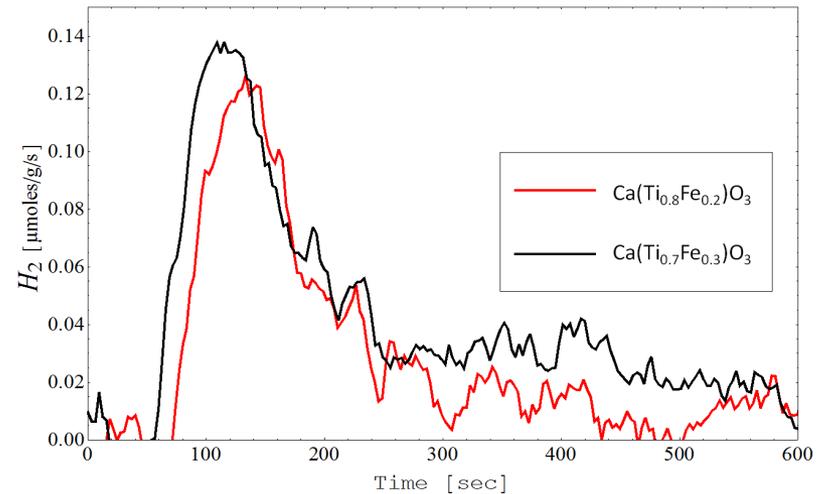


- Assess material behavior at heating rates $> 10^\circ\text{C/s}$.
- Expose material to many rapid heating cycles.

Discovered Perovskite Formulated without Rare-Earth Elements



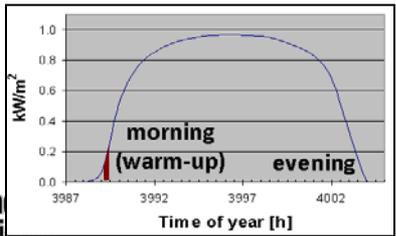
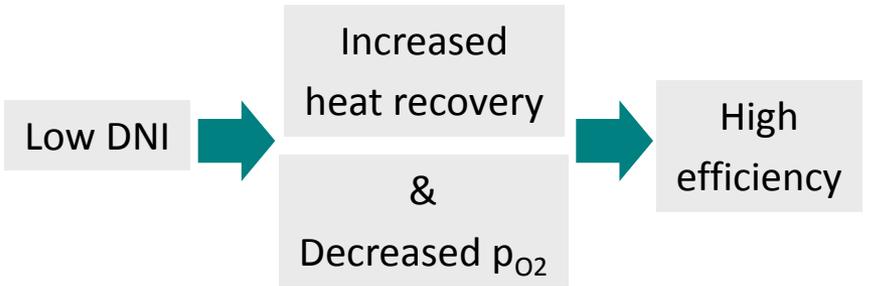
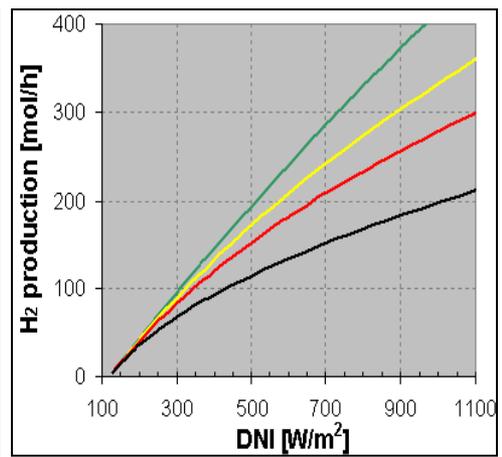
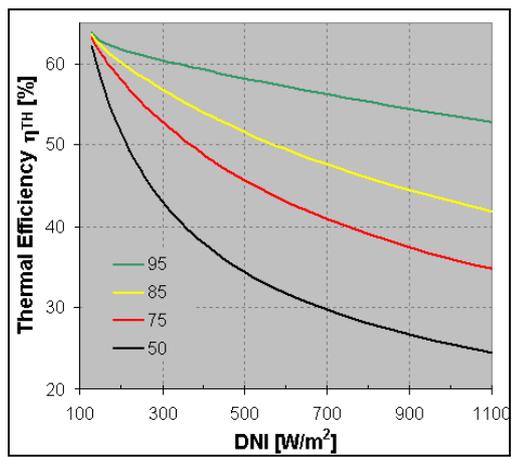
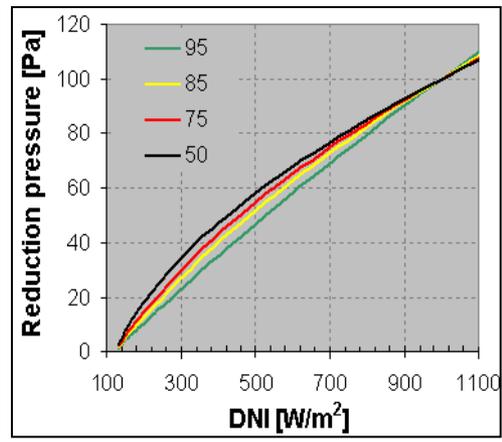
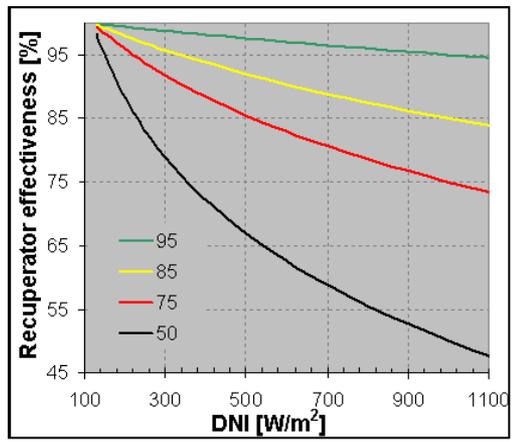
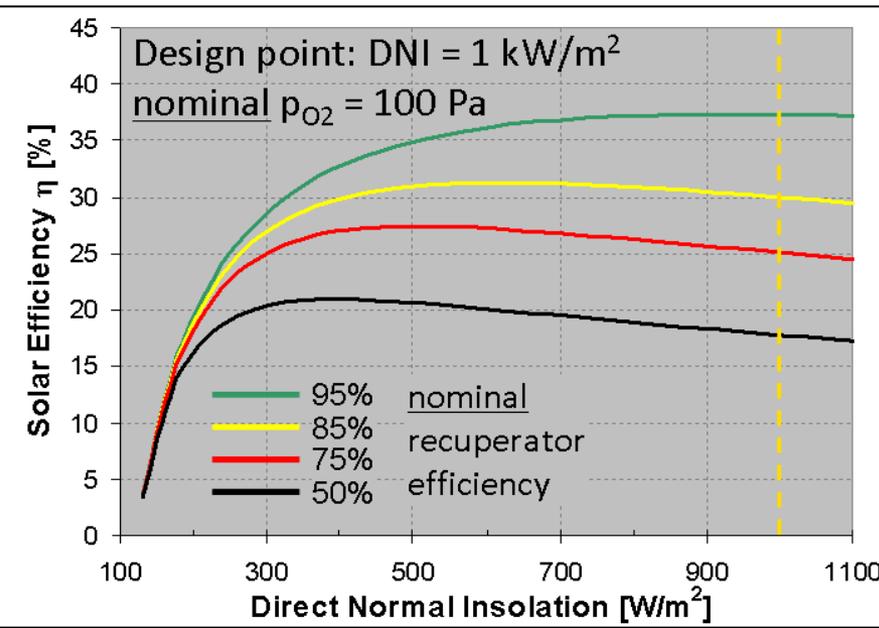
- Perovskite oxygen non-stoichiometry comparable to CeO₂ @ T_R = 1350 °C.



- Perovskite splits H₂O.
- Produce ~5× less H₂ at lower T_R (1350 °C vs. 1500 °C).

- Ca(Ti_xFe_{1-x})O₃ comprised of earth-abundant rock-forming elements.
- Discovery of cheap materials avoids rare-earth market volatility issues.

Sandia Reactor Also Operates Efficiently at Low DNI



- High solar utilization under most operating conditions.
 - 25% solar-to-H₂ annual average efficiency expected
- Use low DNI in the morning for system warm-up.

Prototype Platform Construction and Testing

