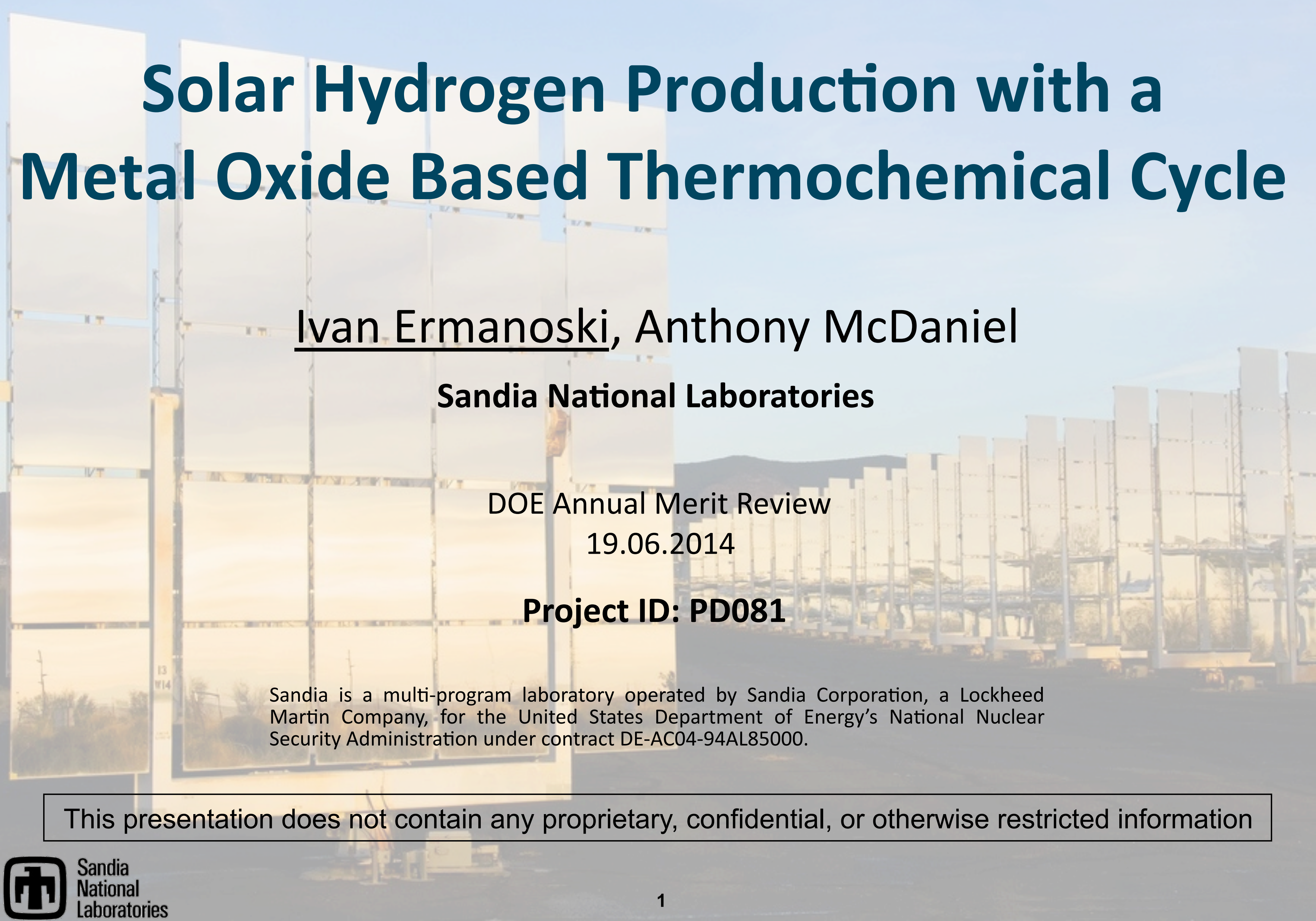

Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

Ivan Ermanoski, Anthony McDaniel

Sandia National Laboratories

DOE Annual Merit Review
19.06.2014

Project ID: PD081

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Overview

Timeline

- Project Start Date: 10/2008
- Project End Date: 10/01/2014*
- Project Complete: TBD

Budget

- Total DOE project value.
  $5487K (2008-2014)
- Funding for FY14.
  $550K (SNL)
- Planned Funding for FY15.
  $650K (SNL)
- Cost share.
  20% contractors, 0% 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

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*Project continuation and direction determined annually by DOE.

Relevance

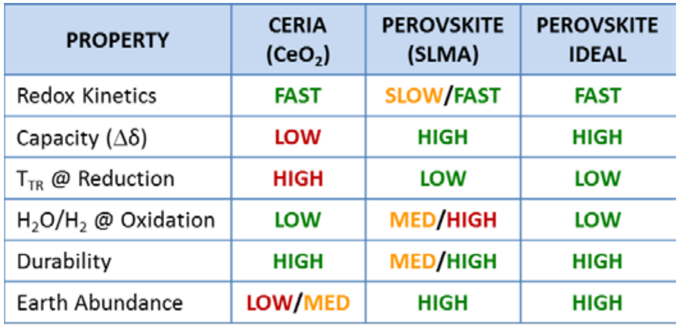
•<u>DOE Objective</u>: By 2015, verify the potential for solar thermochemical (STCH) cycles for hydrogen production to be competitive in the long term and by 2020, develop this technology to produce hydrogen with a projected cost of $3.00/gge at the plant gate.

- **<u>Project Objective</u>: Develop a high-temperature solar-thermochemical reactor and redox materials for *efficient* hydrogen production based on a two-step, non-volatile metal oxide cycle.**
- **2013-2014 Objectives:**
  - Discover and characterize suitable perovskite materials for two-step, non-volatile metal oxide thermochemical cycles.
  - Develop particle receiver-reactor concepts and assess feasibility.
  - Construct and test a reactor prototype.
- **2013 Achievements:**
  - Discovered $Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_3$ (SLMA) perovskite that exhibits better water-splitting (WS) cycle performance than both CeO_2 and ferrites.
  - Demonstrated that oxide reduction under vacuum is the best way to achieve DOE 2020 target for STH efficiency.

Technical Efforts Target Three Key Areas

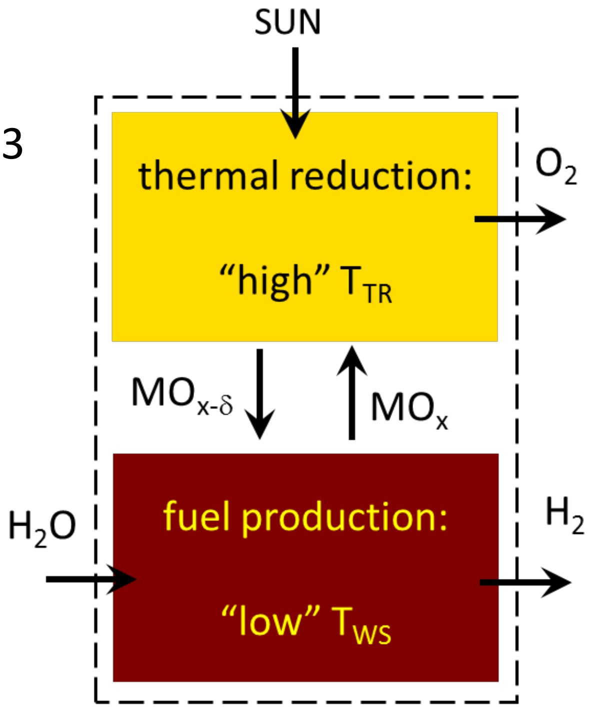
- Systems analysis.
  - Refine estimates for H_2 production cost using H2Av3
- Materials discovery and characterization.
  - Tune material properties with perovskite oxides

a very large composition-property space exists!



PROPERTY	CERIA (CeO_2)	PEROVSKITE (SLMA)	PEROVSKITE IDEAL
Redox Kinetics	FAST	SLOW/FAST	FAST
Capacity ($\Delta\delta$)	LOW	HIGH	HIGH
T_{TR} @ Reduction	HIGH	LOW	LOW
H_2O/H_2 @ Oxidation	LOW	MED/HIGH	LOW
Durability	HIGH	MED/HIGH	HIGH
Earth Abundance	LOW/MED	HIGH	HIGH

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



two-step
metal oxide cycle

- **Three-pronged approach to develop solar thermochemical H_2 production technology that meets all DOE R&D targets.**

Summary of FY13 Reviewer Comments

- Reviewers agree that our FY13 technical approach, facilities, project planning, and achievements were exemplary.
  - Discovery of redox-active perovskite a “major leap forward”
  - Vacuum reduction of oxide a “game changer”
  - “DOE’s goals for hydrogen production costs [seem] achievable”
- Specific programmatic and technical concerns.
  - Research not balanced between material discovery and reactor development
  - High temperature effects on moving reactor parts and particles not addressed
  - Operation at high temperature has not been demonstrated
- Response.
  - Opinions seem to vary, some favor more materials work and less reactor design, others the opposite. We believe the program is well balanced.
  - From a materials viewpoint, two-step water splitting cycles have been demonstrated at high temperature.
  - From a reactor viewpoint, we are methodically marching towards demonstrating high temperature operation in the engineering test stand. Thus far we have not encountered any show stoppers.

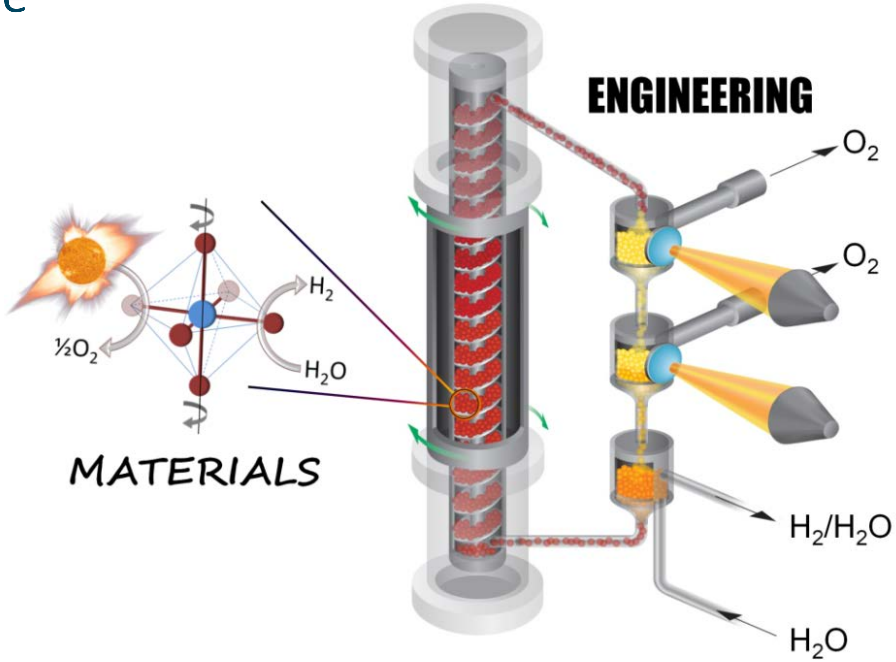
Milestones and Progress

03.2013-03.2014 Accomplishments

ACTIVITY	MILESTONE	COMPLETE
Analyze the hydrogen production cost from a particle reactor on a centralized receiver using the H2Av3 tool.	Analyzed 100,000 kg H_2/day centralized receiver-based facility using CeO_2 and SLMA perovskite oxide, sensitivity analysis reveals reactor efficiency is a critical cost driver. Demonstrated a clear R&D path towards achieving \$2/kg H_2 ultimate cost target for hydrogen production.	**90%**
Synthesize a small number of candidate perovskite oxide redox materials.	Sol-gel method used to synthesize ~2g quantities of 30 perovskite formulations from 7 different Mn- and Fe-based families.	**65%**
Characterize the thermodynamic and kinetic performance of redox materials.	30 new perovskites screened using TGA protocol, conducted detailed kinetic studies on 6 material formulations and hercynite.	**50%**
Derive a thermodynamic model for one SLMA ($Sr_{1-x}La_xMn_{1-y}Al_yO_3$) perovskite compound.	Measured P_{O2}-T-δ for SLMA6464 using TGA and derived a thermodynamic model used to predict STH efficiency in Sandia's particle reactor.	**100%**
Discover redox active perovskites that exceed SLMA performance.	None of the 30 novel perovskite formulations improved the solar-thermochemical H_2 performance baselines established by SLMA (discovered last year).	**50%**
Theoretically analyze Sandia particle reactor performance using SLMA.	Predicted the optimal operating temperature (ΔT), O_2 pressure (vacuum), and heat recovery effectiveness required to meet or exceed a STH conversion ratio greater than the 2020 target of 20%.	**100%**
Design and construct an engineering test stand of particle reactor without solar interface.	Designed, built, and tested a vacuum seal and bearing that enables chamber rotation that can maintain <10 Pa vacuum during full-speed rotation. This is well below the first chamber design pressure of 100 Pa. Finalized designs for major engineering test stand components, complete construction by June.	**60%**
Design central-receiver based H_2 production plant upon which to base H2Av3 analysis.	Designed H_2 production plant including solar field, receiver-reactor, and balance of plant based on SLMA perovskite redox chemistry. Plant sized for 100,000 kg H_2/day.	**90%**

Reactor and Materials Innovation

- We continue to overcome technical barriers to implementing high-temperature solar thermochemical H_2 production.
  - Developed a novel cascading pressure design concept that achieves very low O_2 pressures during reduction.
  - Developed novel perovskite formulations that lower the required thermal reduction temperature.
  - Combined reactor designs and material formulations that achieve optimal STH efficiency.
  - Striving to reduce the dependence on high-temperature solid-solid heat recovery.



- **Advancing solar H_2 production technology through materials and engineering innovation.**

Technical Accomplishments and Progress

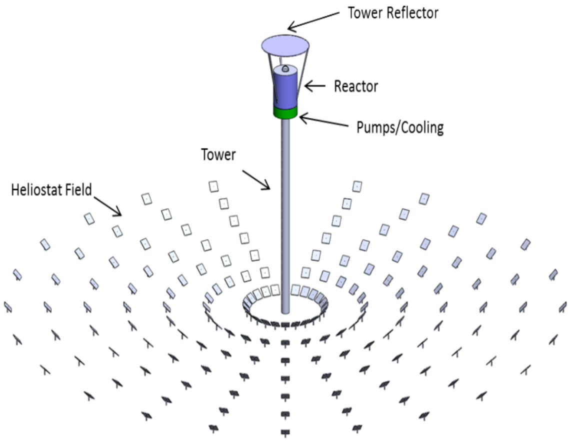
H2Av3 Analysis of 100,000 kg H_2/Day Plant

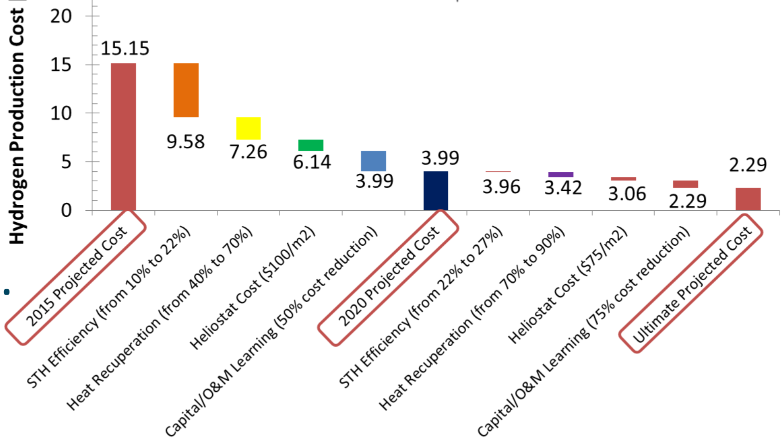
- Central receiver-based particle reactor.
  - 260 towers @ 4.2 MW_{TH}/tower over 3.5 km^2
  - Meteorological data for Daggett, CA
    annual collection efficiency: 51.6%
  - Analyzed 3 cases:
    2015, 2020, and ultimate cost targets
- H_2 cost dominated by capital cost.

DEVELOPMENTAL PROGRESS			
PARAMETER	**2015**	**2020**	**ULTIMATE**
STH Efficiency	10	22	27
Recuperator Efficiency	40%	70%	90%
Heliostat Cost ($/m²)	170	100	75
Capital Reduction Factor*	1.0	0.5	0.25
O&M Reduction Factor	1.0	0.5	0.25
H_2 Cost ($/kg)	15.15	3.99	2.29

*Excluding heliostat cost.

- Ultimate cost target of ~$2/kg H_2 achieved.
  - STH efficiency of 27%
  - 75% decrease in capital *and* O&M costs relative to 2015 case



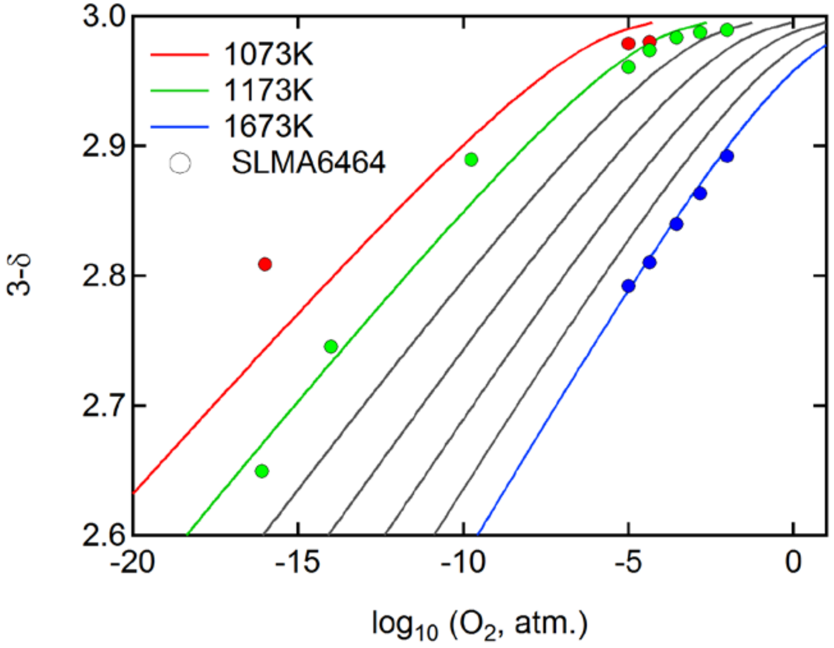


- **STH efficiency linked to capital cost (i.e., determines number of heliostats, towers, particle reactors, heat exchangers, etc.).**
- **High STH efficiency critically important to meeting DOE cost targets.**

Thermodynamic Model for SLMA

- P_{O2}-δ-T relationship measured using TGA.
  - 18 orders of magnitude in P_{O2}
  - 1073K < T < 1673K
  - $0 < \delta < 0.35$
- O_2-SLMA solid solution model.
  - Electrons delocalized
  - O-vacancies randomly distributed
  - Non-ideal $\Delta H_{oxid}(\delta)$
- Fit ΔH_{oxid}, ΔS_{oxid}, and '*a*' to P_{O2}, δ, and T.

$$MO_{3-\delta_i} + \frac{(\delta_i - \delta_f)}{2} O_2 \rightarrow MO_{3-\delta_f}$$



$$\frac{RT}{2}\ln P_{O2} = \Delta H^0_{oxid} - a\delta - T\left(\Delta S^0_{oxid} + R\ln\left(\frac{\delta}{3-\delta}\right)\right)$$

δ is a measure of oxygen deficiency in $ABO_{3-\delta}$ perovskites

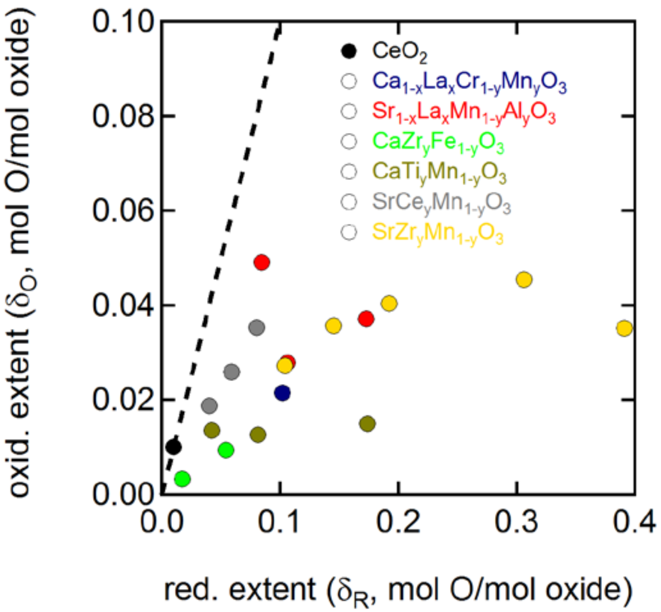
- **Model predicts high STH efficiency for SLMA in Sandia's particle reactor.**
- **$\delta > 0.3$ for SLMA uncommonly large (yields high H_2 capacity).**

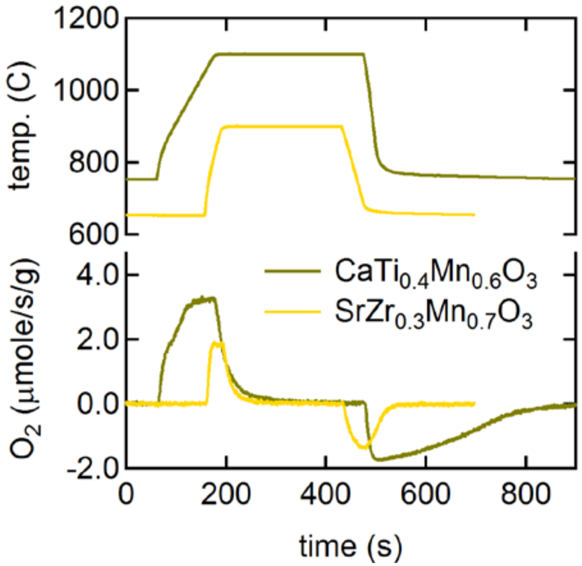
Sandia National Laboratories

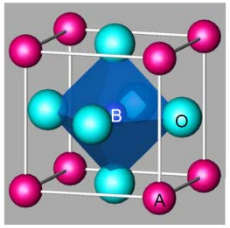
The Search Continues for a Perovskite

- Synthesized 30 perovskites from Mn- and Fe-based B-site families.
  - Sol-gel method
- Identified promising candidates using TGA screening.
  - T_{TR}=1350°C for 1.5 hr in Ar
  - T_{WS}=1000°C for 1.5 hr, 40 vol.% H_2O
- Detailed kinetic measurements on 6 materials in Sandia's laser-heated stagnation flow reactor (SFR).
  - Onset temperature for reduction
  - O_2 uptake-and-release
  - Water-splitting (WS) activity

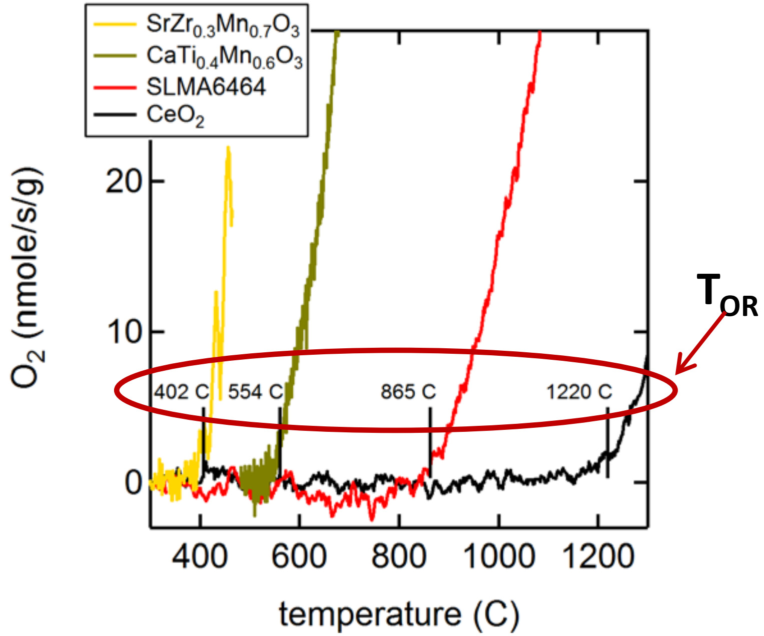
- **Found several redox-active perovskites with T_{TR} < CeO_2 and δ > CeO_2.**



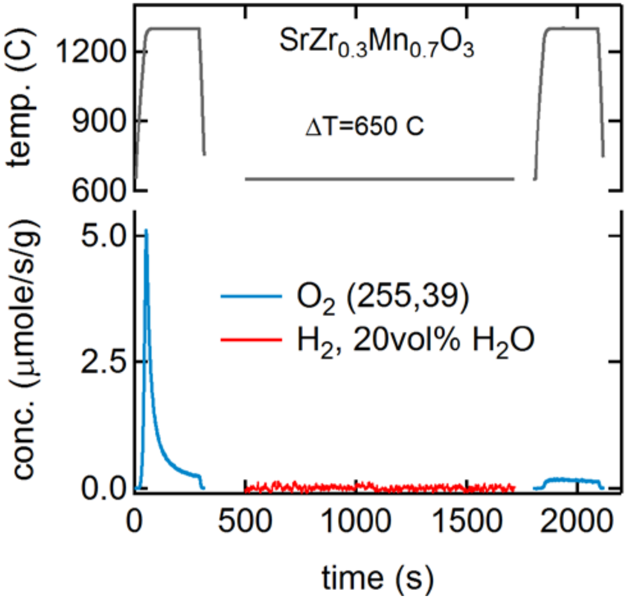




Established Threshold for Reduction Temperature



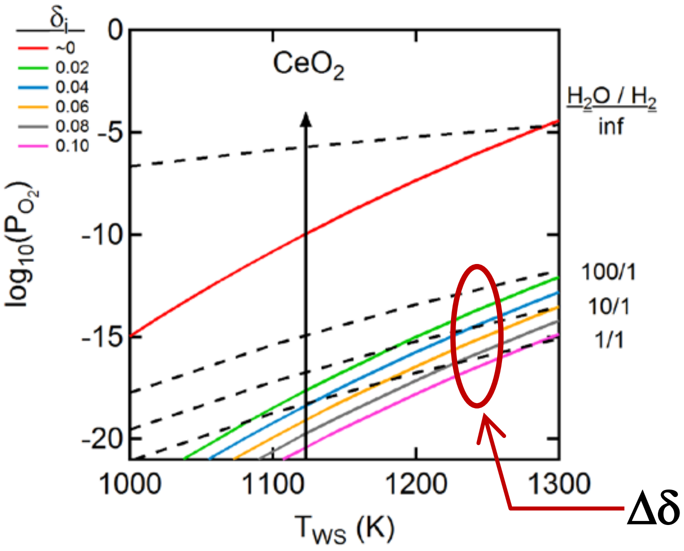
- T_{OR} = O_2 onset temperature for thermal reduction.
  - Different than T_{TR} (usually $T_{OR} << T_{TR}$)
- Mn-based perovskites found with very low T_{OR}.
  - Implies $\Delta H_{reduction} << 450$ kJ/mol O



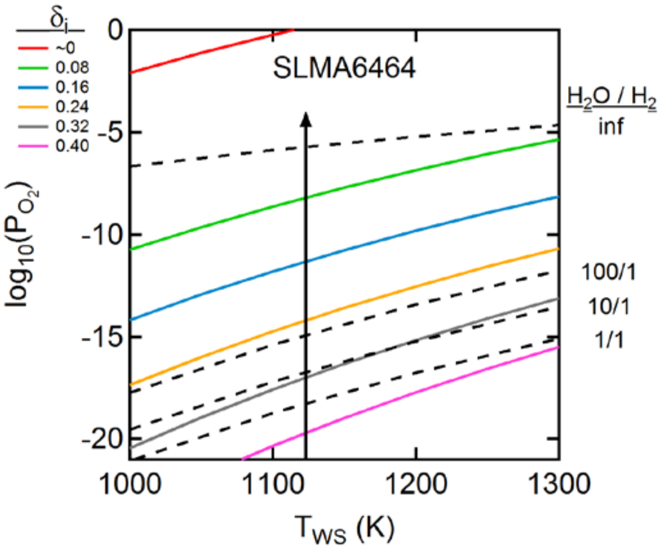
- If T_{OR} < 850°C, then WS unfavorable or inefficient.
  - SFR data show O_2 during thermal reduction but no H_2 during WS
  - High H_2O/H_2 ratio required for re-oxidation

- **Mn-based perovskites yield large δ.**
- **Need to raise T_{OR} above 865°C (SLMA's).**

Ideal Material Bracketed Between CeO_2 and SLMA



IDEAL:
850°C<T_{OR}<1200°C
750°C<T_{WS}<900°C
$\Delta\delta$ ~ 0.3
$H_2O/H_2 < 20$
$Rate_{WS}$ ~ CeO_2



η_{STH} limited by oxide heating.

Optimal η_{STH}.

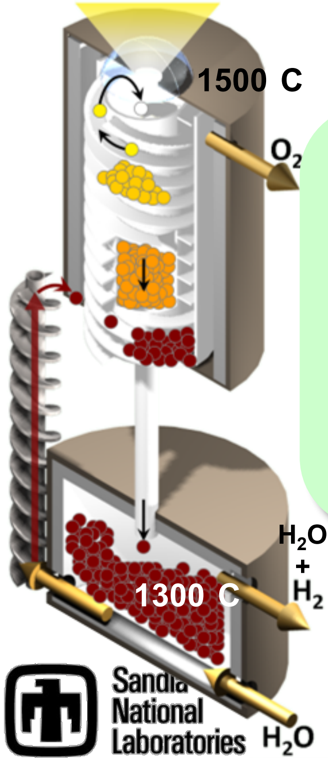
η_{STH} limited by steam heating.

- Thermodynamics determine favorable *and* efficient WS conditions:
  - ΔH and ΔS strong functions of composition (δ) for non-stoichiometric oxides
- Desirable to span the largest possible Δδ range with lowest H_2O/H_2 ratio.

- **We are confident that a perovskite can be found that will achieve the DOE 2020 STH efficiency target.**

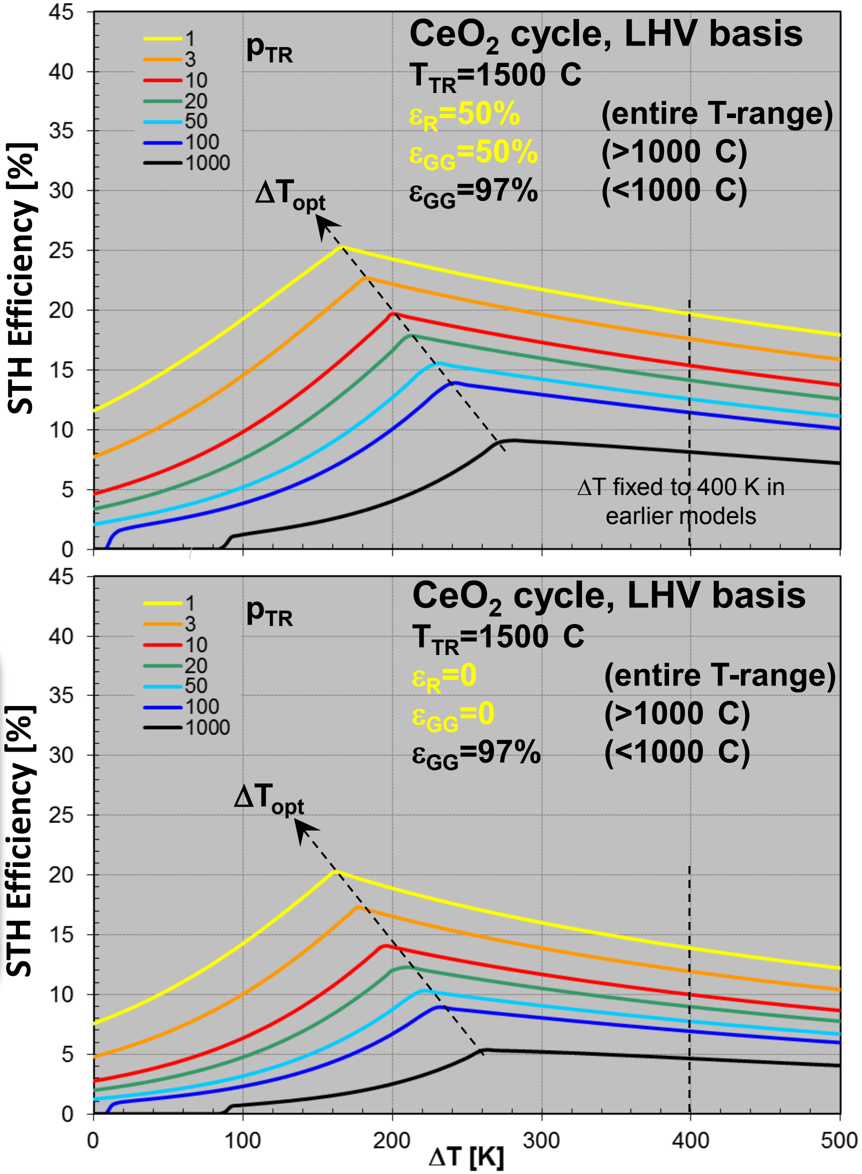
Maximizing Efficiency: Improved Models to Target Optimal Operation

- Issue: Large fixed ΔT (T_{TR}-T_{WS}) not optimal.
- Solution: Comprehensive efficiency model developed to identify optimal conditions. Includes losses and ALL mechanical work.
- Result: Higher efficiency possible at ΔT_{opt}.
- No credit taken for high-quality waste heat.



- **DOE 20% STH efficiency target achievable in CeO_2 cycle at:**
  - **p_{TR}<10 Pa**
  - **T_{TR}=1500°C**
  - **T_{WS}~1300°C**
  - **heat recovery at T>1000°C**

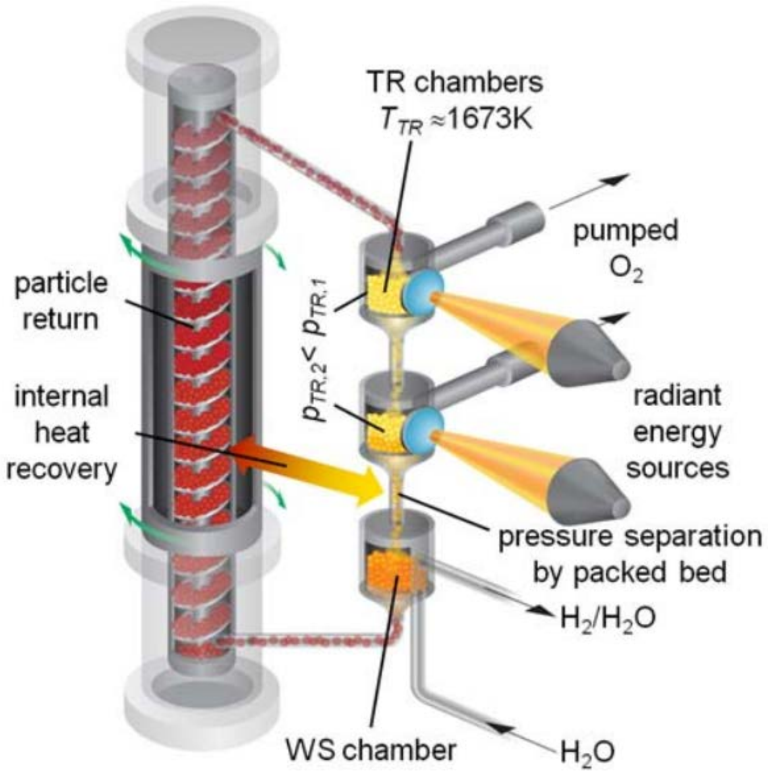
✓

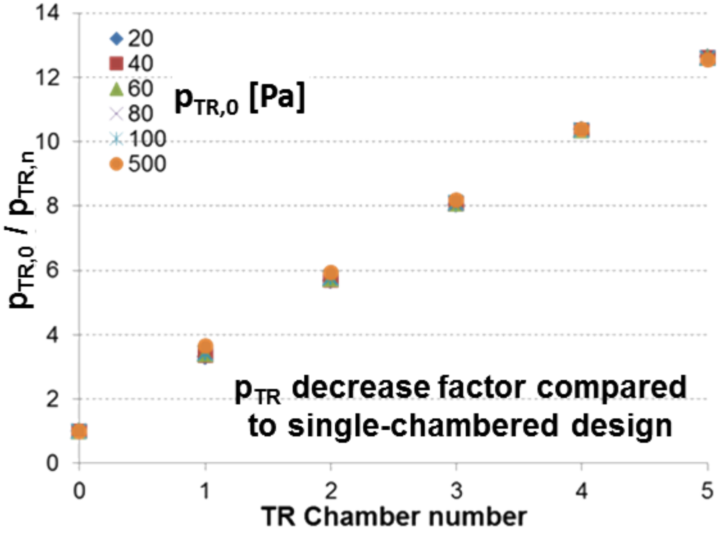


I. Ermanoski, J. E. Miller and M. D. Allendorf, *Physical Chemistry Chemical Physics*, 2014, 16, 8418

Maximizing Efficiency: Advancing Reactor Design to Lower p_{TR}

- Challenge: Large volumetric O_2 flows at low p_{TR} exceed practical pumping speeds.
- Solution: An improved, cascading pressure design, with multiple thermal reduction chambers at successively lower p_{TR}.
- Result: >10x lower achievable p_{TR}.
- Our existing moving packed particle bed concept ideally suited for a practical pressure cascade implementation.

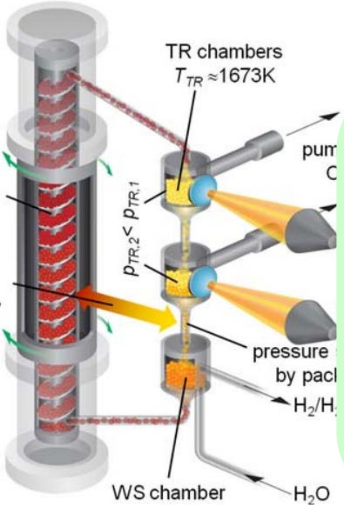




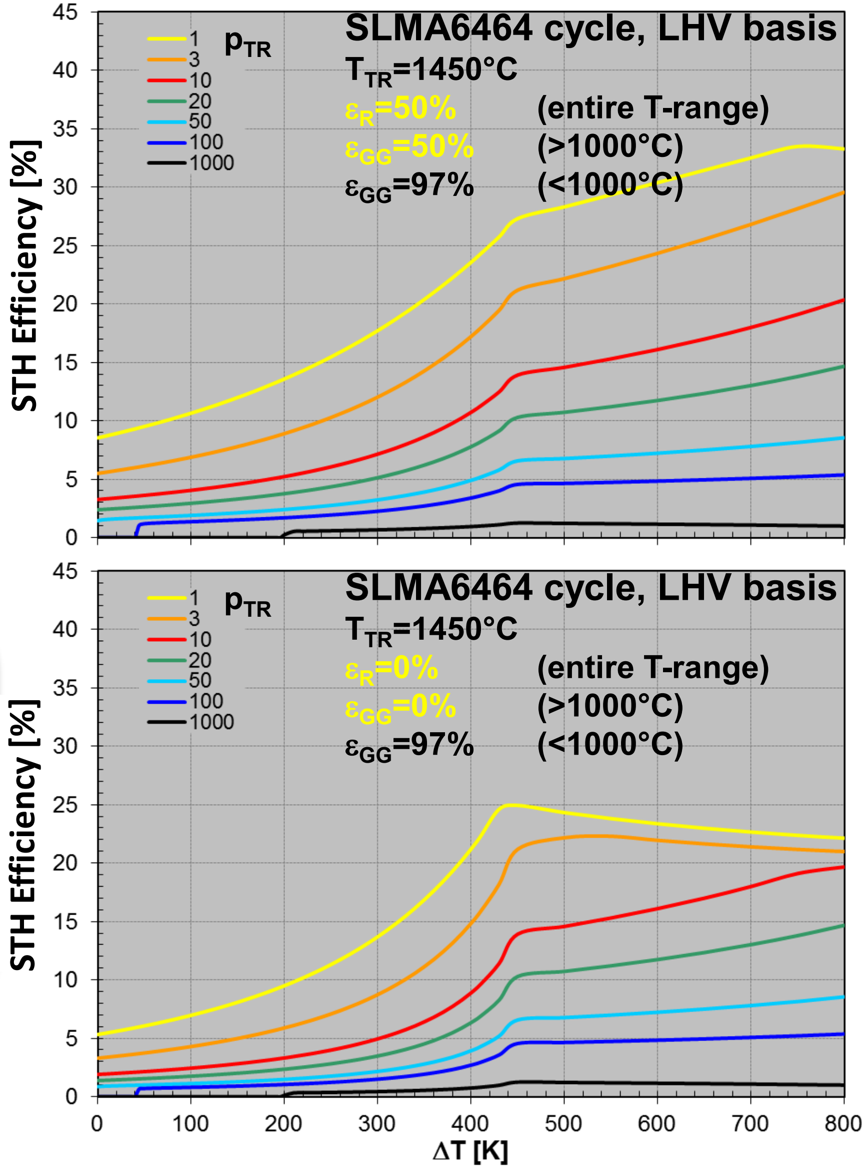
- **Required p_{TR}<10 Pa comfortably achievable in a cascading pressure design.**

Maximizing Efficiency: Combining Advanced Materials and Reactors

- Ceria challenges: High T_{TR}=1500°C; High optimal T_{WS}~1300°C; High-T heat recovery required (solid and gas).
- Solution: Replace ceria with SLMA materials.
- Result: High efficiency achievable under much less demanding conditions.

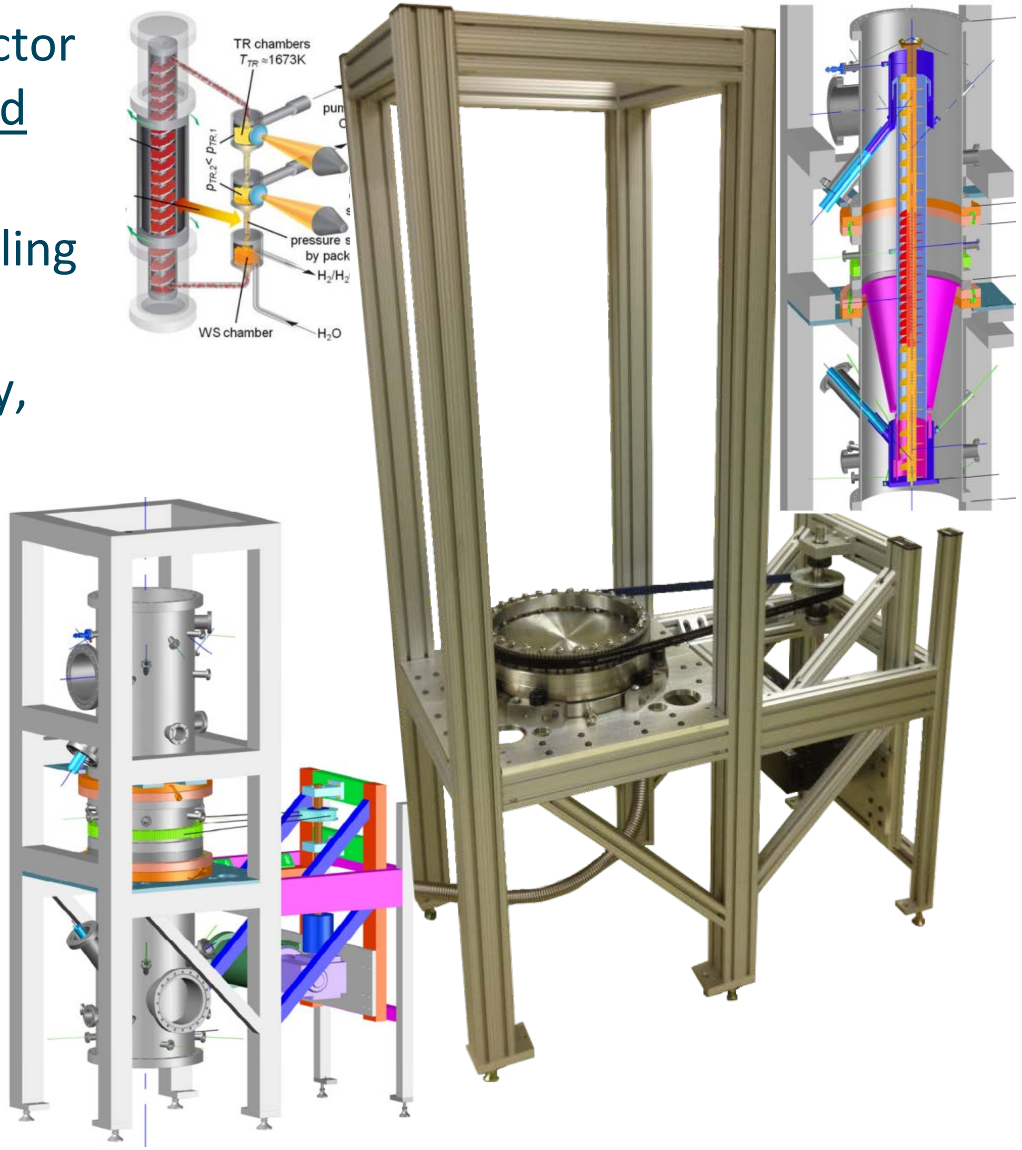


- **DOE 20% STH efficiency achievable in SLMA6464 cycle at:**
  - p_{TR}<10 Pa
  - T_{TR}=1450°C
  - T_{WS}~800°C-1000°C
  - NO high-T heat recovery



Engineering Test Stand Design and Construction

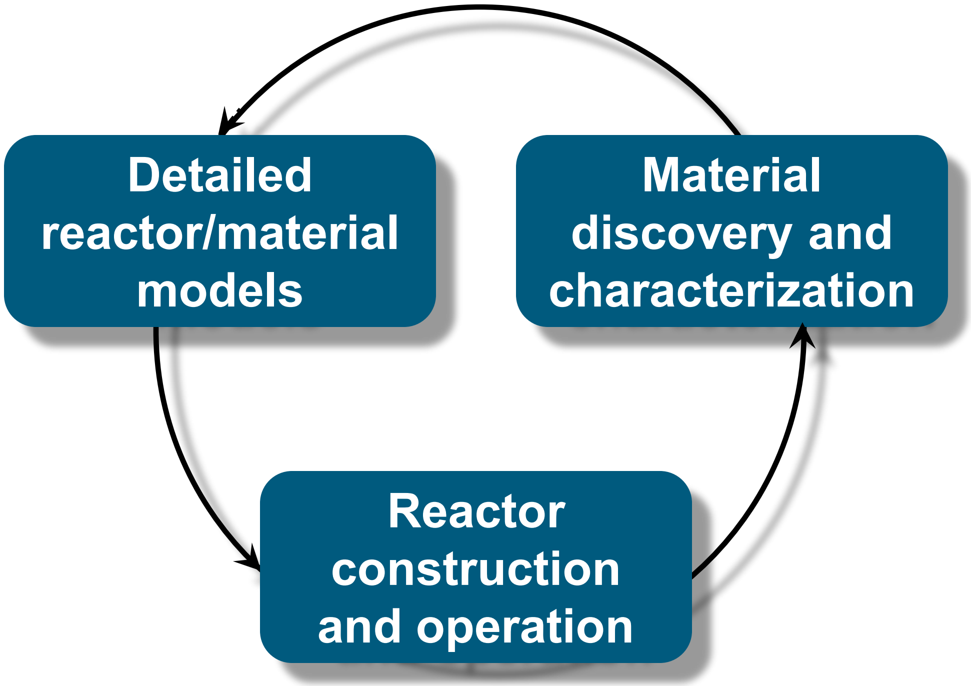
- Gen. 2 test stand to evaluate key reactor concepts under vacuum and increased temperature conditions.
- Design adapted to most recent modeling and material developments.
- Design compatible with heat recovery, but emphasis on low p_{TR}.
- Will become part of a fully functional reactor.



- **Large rotary vacuum seals successfully tested to pressures well below those required in reactor operation.** ✓

Toward the Limits: Reactor-Material Design Synergy

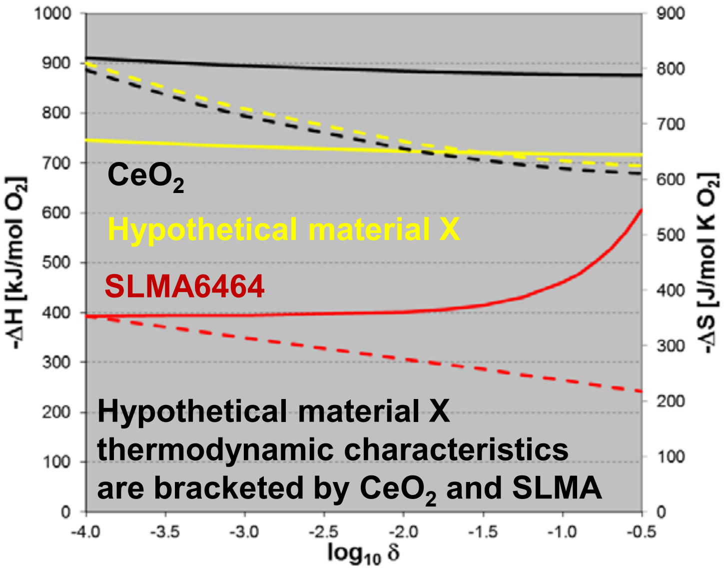
- Q: How to realize the full efficiency potential of solar-thermochemical H_2 production?
- A: By concurrent and intimately coupled reactor and material development.



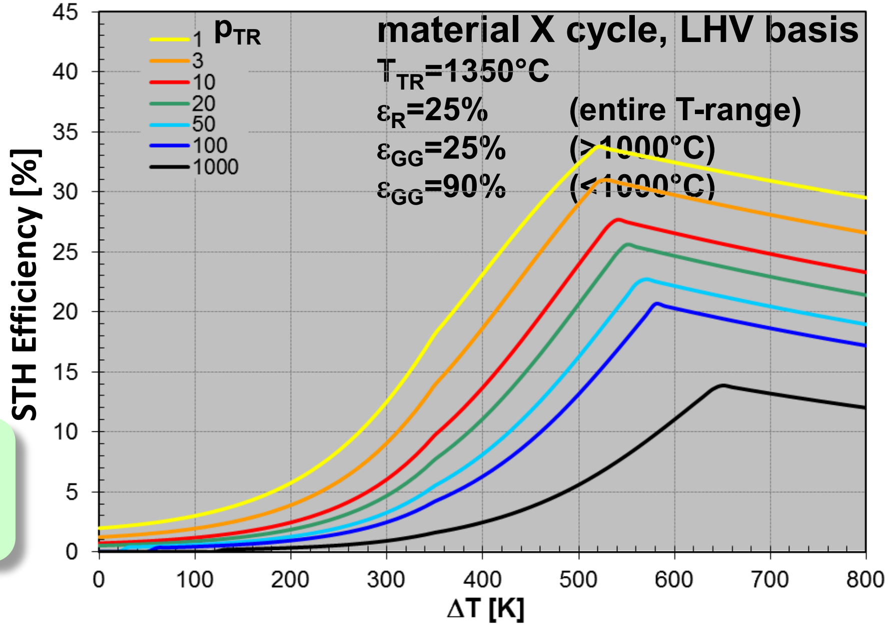
Detailed reactor/material models

Material discovery and characterization

Reactor construction and operation



Hypothetical material X thermodynamic characteristics are bracketed by CeO_2 and SLMA



material X cycle, LHV basis

T_{TR}=1350°C

ε_R=25% (entire T-range)

ε_{GG}=25% (>1000°C)

ε_{GG}=90% (<1000°C)

- **When suitable materials are found STH efficiency ~25-35% will be feasible.**

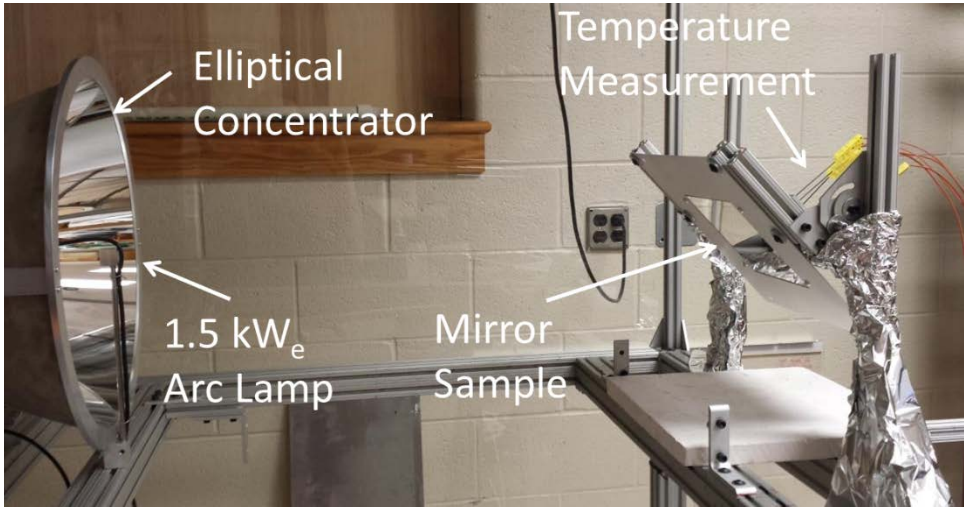
High Flux Mirror Testing for Beam-Down Optic

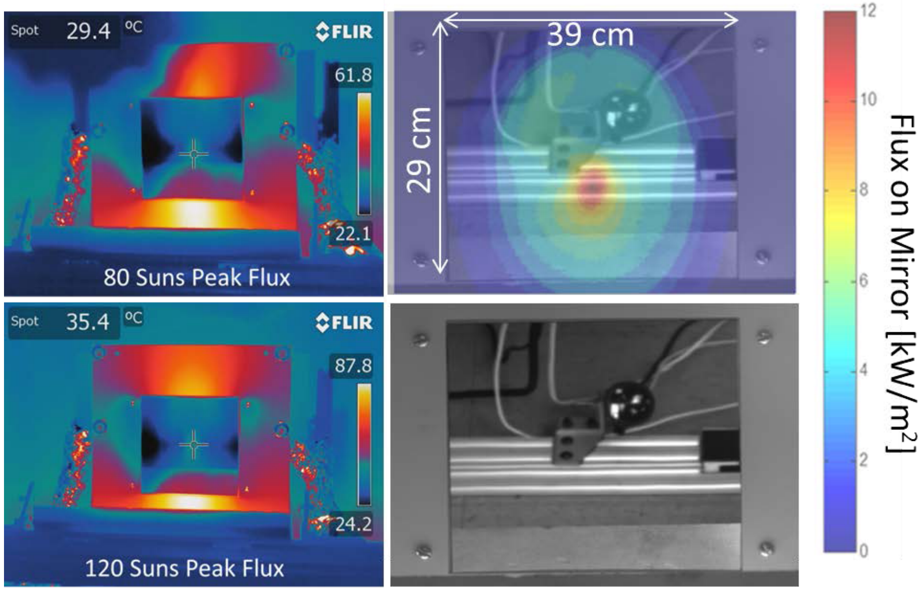
- 1 mm back-silvered heliostat mirror.
  - Bonded to a simple water-cooled heat exchanger
- Two flux levels tested.
  - 80 and 120 suns
  - Non-uniform solar flux
  - Temperatures measured with thermocouples and IR camera

LOCATION	80 SUNS	120 SUNS
	TEMP (°C)	
Mirror Center Surface	29.4	35.4
Max Back Side	22.3	27.0
Min Back Side	21.2	23.5
Water Coolant	17.5	17.5

- **Water cooled beam-down optic operates successfully at high solar flux.**

Bucknell's solar simulator





FY14 Collaborations

- 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 both Sandia and CU materials

    Dr. Darwin Arifin, completed his PhD thesis at Sandia

    Mr. Chris Muhich and Ms. Kayla Weston, hercynite studies

Proposed Future Work

Dependent on continued DOE out year funding:

- Material discovery, screening, and characterization using theory and experiment.
  - Continue with perovskites
  - Investigate non-ferrite metal oxides undergoing a solid-solid phase change that liberates oxygen (a new direction)
  - Develop a solid-state coulometric titration experiment for measuring thermodynamic data on new redox active materials
- Implement a durability testing protocol for redox active materials.
  - Develop an experimental platform for rapid cycling and aging studies
- Integrate multiple thermal reduction chambers and a solar interface into the engineering test stand.
- Expand Sandia’s theoretical efficiency model to allow exploration/optimization of ideal materials and integrate solar receiver configurations.
  - Increase the fidelity of subcomponent models
- Design centralized tower and field configurations compatible with multiple thermal reduction chambers.
  - Evaluate beam-down vs. beam-up optics

Summary

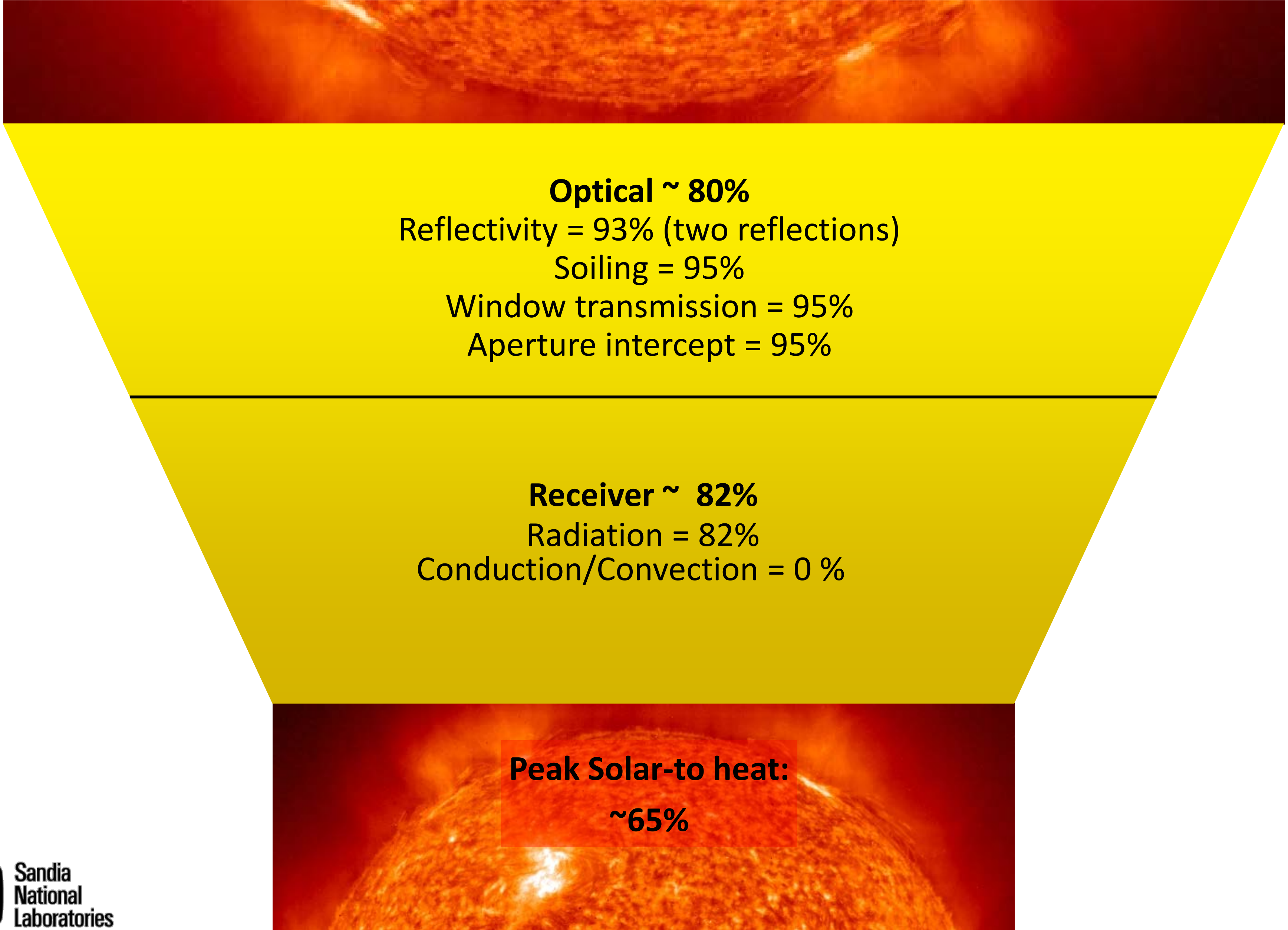
- Analyzed H_2 production costs for a centralized receiver-based particle reactor.
  - 100,000 kg H_2/day, DOE's ultimate cost targets are achievable
  - Sensitivity analysis reveals the importance of STH efficiency
- Discovered more redox active Mn- and Fe- based perovskite formulations .
  - Synthesized and screened 30 compounds, none perform better than SLMA
- Established and refined material performance metrics.
  - Ideal material behavior is bracketed by two existing compounds, CeO_2 and SLMA.
- Developed a novel cascading pressure reactor concept that enables ultra low vacuum during reduction.
- Analyzed efficiency of Sandia particle reactor under various operating conditions.
  - Identified operating conditions that establish optimal η_{STH} for CeO_2 and SLMA.
  - Determined that DOE 2020 technical targets for STCH can be achieved in a two-step high temperature thermochemical cycle.
- Continue to refine the design requirements for a beam-down optical system for particle reactor operating at ~5 MW_{TH}.

FY14 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.

Technical Backup

Technical Back-Up Slides

System Level View



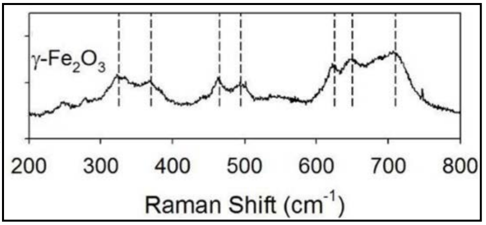
Optical ~ 80%
Reflectivity = 93% (two reflections)
Soiling = 95%
Window transmission = 95%
Aperture intercept = 95%

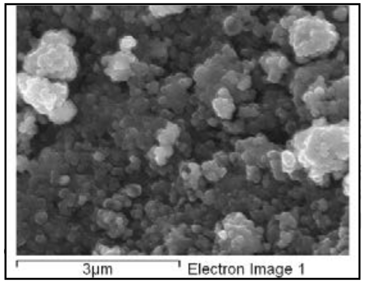
Receiver ~ 82%
Radiation = 82%
Conduction/Convection = 0 %

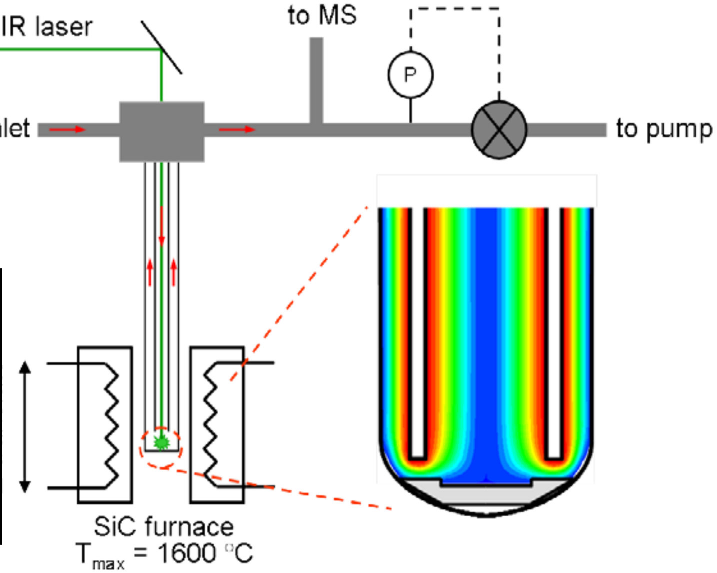
Peak Solar-to heat:
~65%

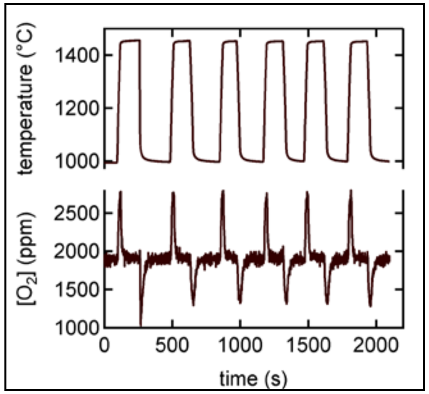
Experimental Methods for Characterizing Redox Materials

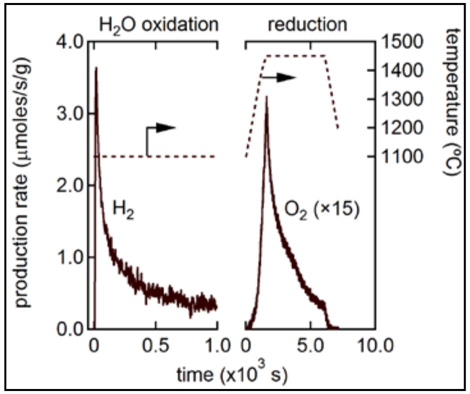
- Surface analysis.
  - Surface Raman, XPS
- Material properties.
  - BET surface area
  - SEM-EDX, TEM-EELS, XRD
- Kinetic measurements.
  - Stagnation flow reactor
    - 500 W CW NIR laser heatin
    - Modulated beam mass spectrometer
- Screen for O_2 uptake and release.
  - Assess redox viability
- Resolve thermal reduction behavior.
- Resolve water splitting behavior.
  - Variable T, P, $[H_2O]$
- Analysis.
  - Resolve rate limiting mechanisms
  - Develop kinetic models
  - Evaluate material stability
  - Test cycle performance



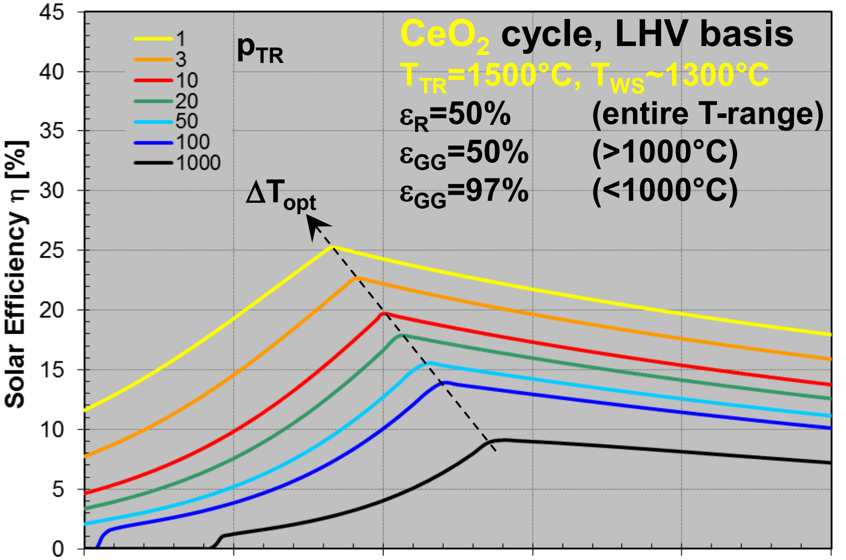








Ceria vs. SLMA6464: Efficiency Comparison



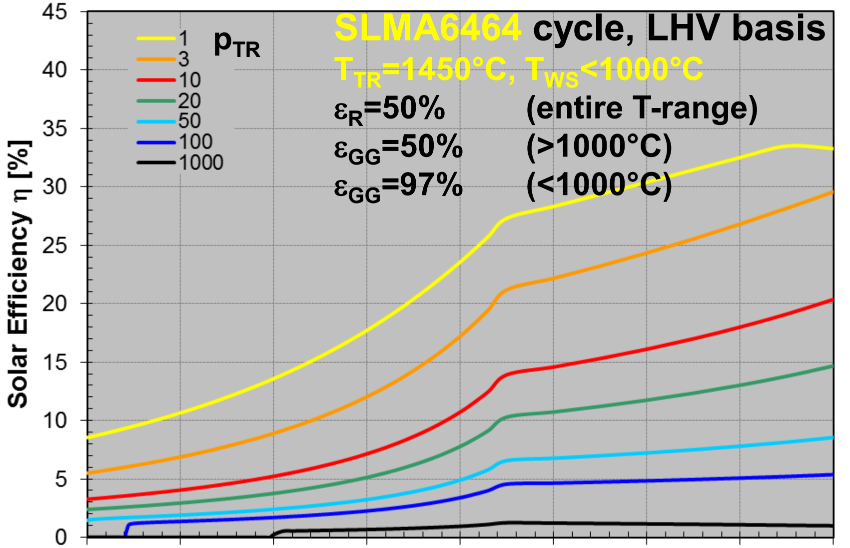
CeO_2 cycle, LHV basis

T_{TR}=1500°C, T_{WS}~1300°C

ε_R=50% (entire T-range)

ε_{GG}=50% (>1000°C)

ε_{GG}=97% (<1000°C)



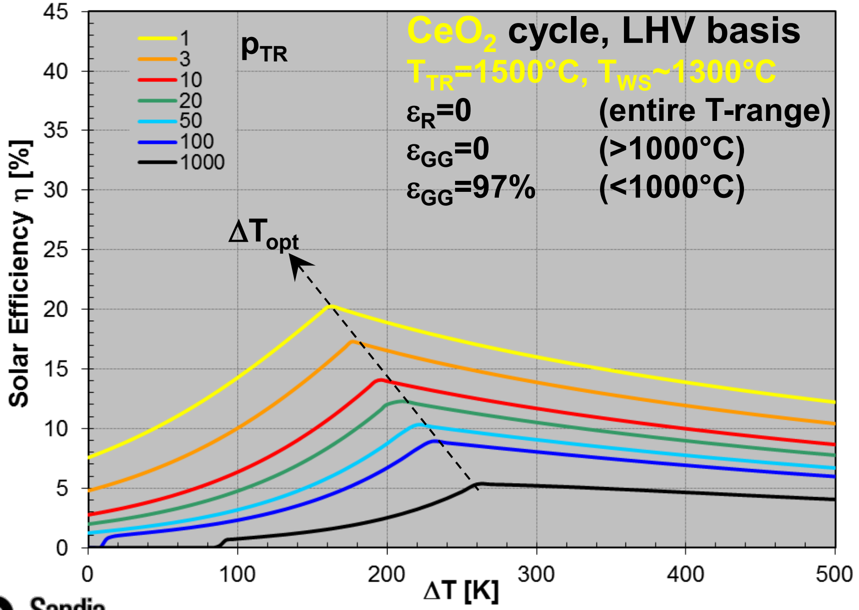
SLMA6464 cycle, LHV basis

T_{TR}=1450°C, T_{WS}<1000°C

ε_R=50% (entire T-range)

ε_{GG}=50% (>1000°C)

ε_{GG}=97% (<1000°C)



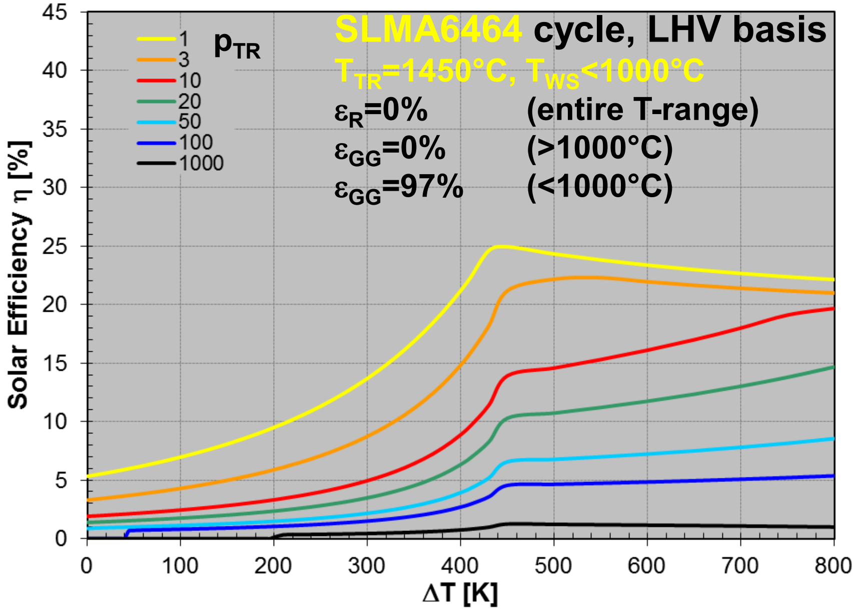
CeO_2 cycle, LHV basis

T_{TR}=1500°C, T_{WS}~1300°C

ε_R=0 (entire T-range)

ε_{GG}=0 (>1000°C)

ε_{GG}=97% (<1000°C)



SLMA6464 cycle, LHV basis

T_{TR}=1450°C, T_{WS}<1000°C

ε_R=0% (entire T-range)

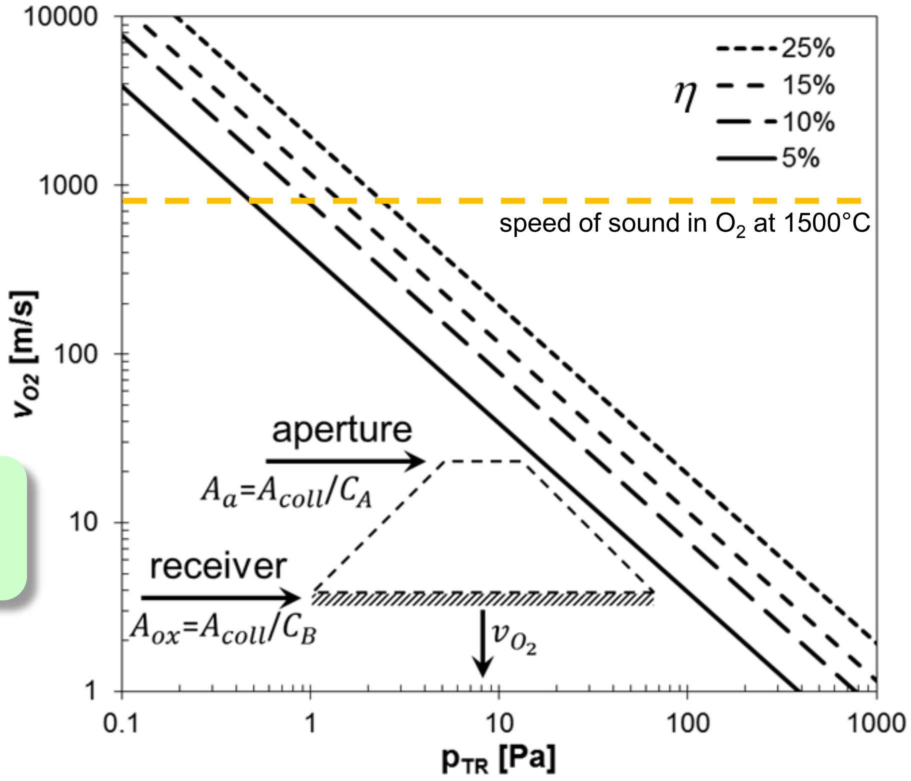
ε_{GG}=0% (>1000°C)

ε_{GG}=97% (<1000°C)

Pumping Limitations in a Single-Chambered Reactor

- Thermal reduction pressure, p_{TR}, is limited by the O_2 flow speed when pumped out of the thermal reduction chamber(s).
- In a single-chambered design, this limits p_{TR} to values above 10 Pa.

$$v_{O_2} = \frac{\eta C_B R T_{TR} * \dot{Q}_S}{2 * HHV_{H2}} \frac{1}{p_{TR}}$$

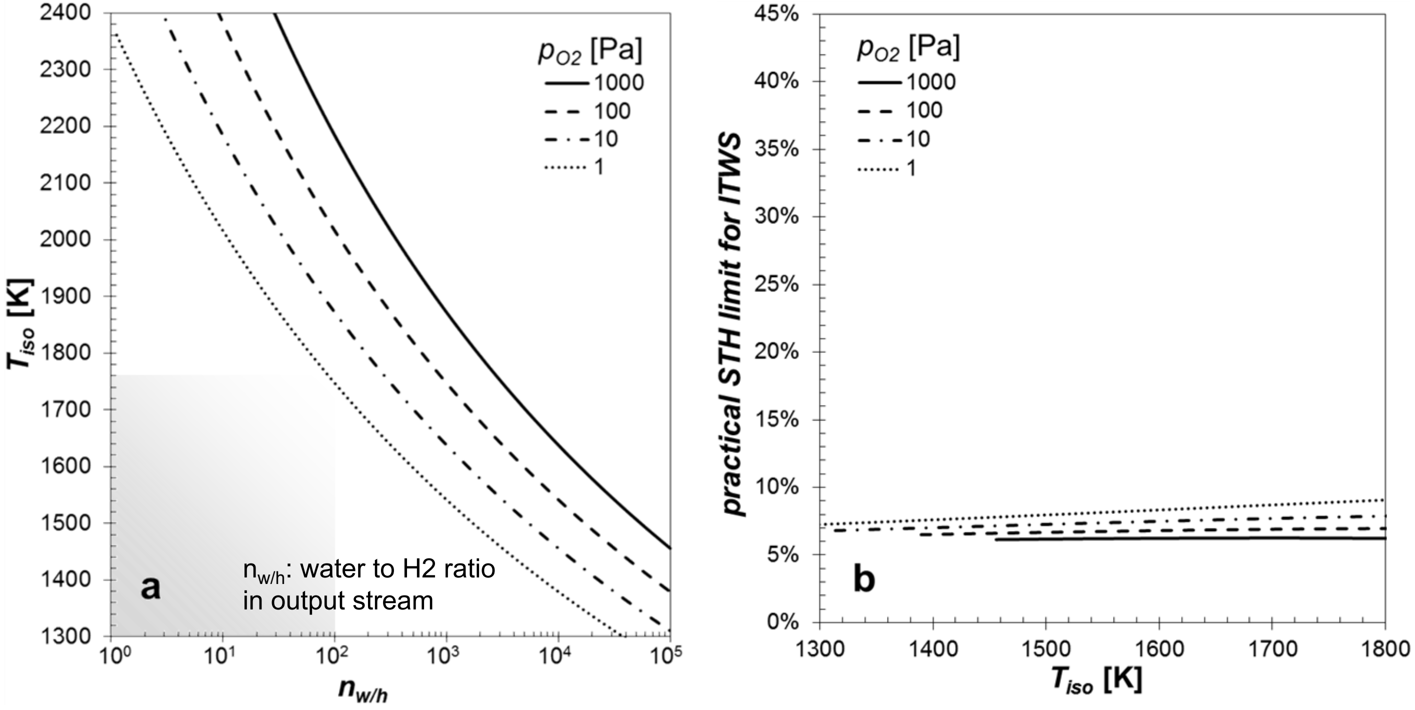


- **Multi-chambered cascading pressure design required to achieve low p_{TR}.**

Isothermal Water Splitting (ITWS)

- ITWS can be described using solely water thermodynamics, with no material or reactor assumptions:

$$T_{iso} = \frac{-\Delta H^{\circ}_{H2O}}{R\left(ln\left(p_{O_2}^{1/2}\right) - ln\left(\frac{p_{H_2O}}{p_{H_2}}\right)\right) - \Delta S^{\circ}_{H2O}}$$



$n_{w/h}$: water to H2 ratio in output stream

- **Seemingly easier, ITWS is challenging and inefficient**

I. Ermanoski, J. E. Miller and M. D. Allendorf, *Physical Chemistry Chemical Physics*, 2014, 16, 8418