Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

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DOE Annual Merit Review
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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: 10/01/2012*
- Project Complete: 75%

Barriers Addressed

- U: High temperature thermochemical technology.
- V: High temperature robust materials.
- X: Coupling solar and thermochemical cycles.

Budget

- Total project funding to date
  DOE share: $4002K (2008-2012)
  Contractor share: $548K
- Funding for FY11
  $175K (SNL)
- Planned Funding for FY12
  $625K (SNL ~$408K) (CU ~$217K)

Partners

- University of Colorado, Boulder CO
  Prof. Alan Weimer
  Mr. Darwin Arifin
- Bucknell University, Lewisburg PA
  Prof. Nathan Siegel

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*Project continuation and direction determined annually by DOE.

Relevance

•DOE Objective: Develop high-temperature thermochemical cycles driven by concentrated solar energy to produce hydrogen that meet the DOE threshold cost goal of <$2.00/gge at plant gate.

- **Project Objective: Develop a high-temperature solar-thermochemical reactor for efficient hydrogen production. The successful development of this reactor will provide a solar interface for most two-step, non-volatile metal oxide cycles.**

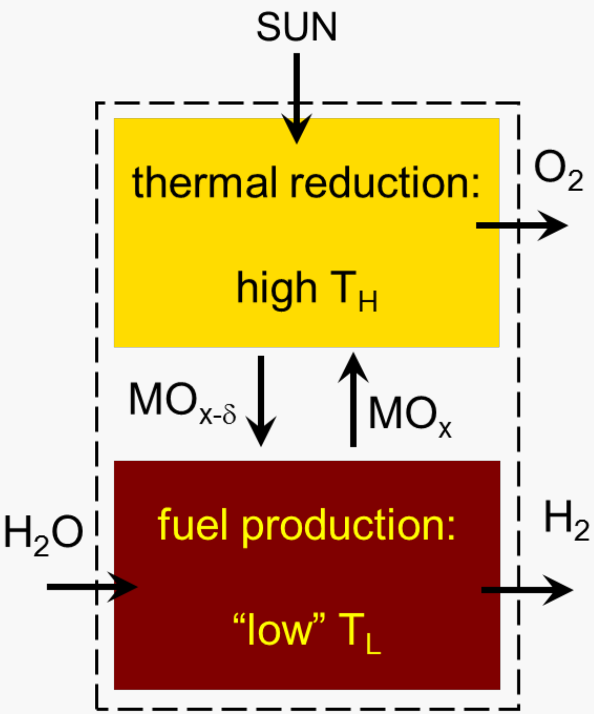
- **2011-2012 Objectives:**
  - Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical cycles.
  - Establish a screening protocol for candidate reactive materials and structures.
  - Design particle receiver-reactor concepts and assess feasibility.
  - Construct and test reactor prototypes.

Technical Efforts Target Three Key Areas

- Materials discovery and characterization.

property	ferrite (Fe_2O_3)	ceria (CeO_2)	hercynite ($FeAl_2O_4$)	perovskite (ABO_3)	ideal
redox kinetics	**SLOW**	**FAST**	**SLOW/MED**	**?**	**FAST**
redox capacity	**HIGH**	**LOW**	**HIGH**	**HIGH**	**HIGH**
reduction T_H	**MED/HIGH**	**HIGH**	**MEDIUM**	**LOW**	**LOW**
durability	**MEDIUM**	**HIGH**	**HIGH**	**?**	**HIGH**
earth abundance	**HIGH**	**LOW/MED**	**HIGH**	**?**	**HIGH**

- Reactor design and development.
  - Direct solar absorption by redox material
  - Efficient heat recovery between T_H and T_L >75%
  - Continuous ON-SUN operation
  - Intrinsic gas and pressure separation (H_2 from O_2)
- Systems analysis.
  - Derive REALISTIC estimate for H_2 production cost
  - THEORETICAL performance must meet DOE cost targets



Two-step
metal oxide cycle

- **MATERIAL and REACTOR DESIGN are critically linked.**
- **Good reactor design compensates for non-ideal material.**

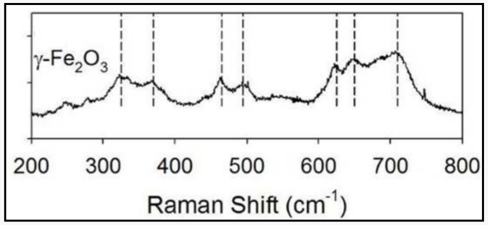
Milestones and Progress

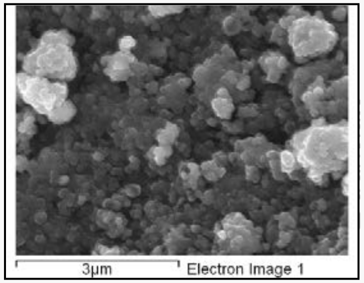
03.2011-03.2012 Accomplishments

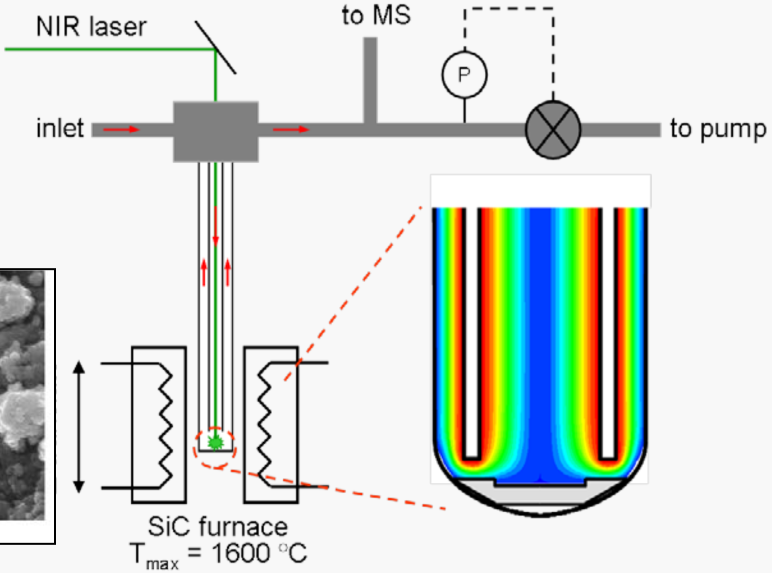
ACTIVITY	MILESTONE	COMPLETE
Develop a protocol for material characterization	evaluated oxidation behavior (water splitting) of ferrite, ceria, and hercynite cycles	**50%**
Develop and validate a kinetic model for ceria	model used to establish theoretical cycle performance metrics for ceria in Sandia reactors	**100%**
Synthesize and characterize doped ceria materials	decreased thermal reduction temperature for ceria (T_H) below 1450°C	**50%**
Theoretically analyze particle reactor performance	demonstrated that Sandia particle reactor has the potential to achieve >30% solar-to-H_2 thermal efficiency	**100%**
Design and test particle conveyor concept	validated conveyor concept by demonstrating a sustained mass flow rate of 30 g/s particles for 1 hour	**100%**
Evaluate reactor materials for high-temperature chemical compatibility with ceria, with no adverse reactivity, during lab-scale, short duration tests	no reactivity with Al_2O_3 at 1550°C after 3 hours no reactivity with SiC at 1400°C after 3 hours no reactivity with coated SiC at 1450°C after 3 hours	**75%**
Design, construct, and test a “cold” reactor prototype	demonstrate mechanical operation at T < 200°C for 10 hours	**30%**

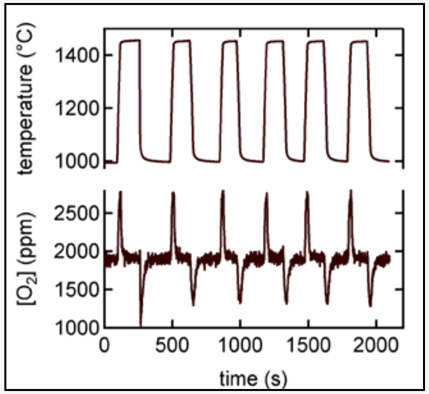
Experimental Methods for Characterizing Redox Materials

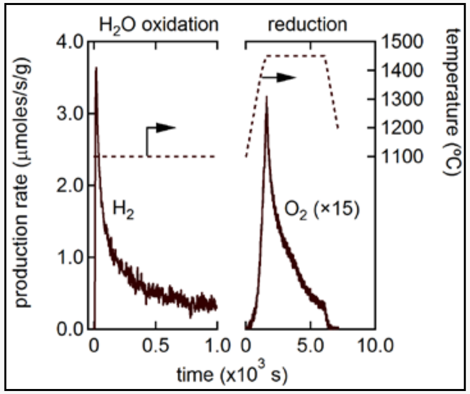
- Surface analysis.
  - Surface Raman, XPS
- Material properties.
  - BET surface area
  - SEM-EDX, TEM-EELS, XRD
- Kinetic measurements.
  - Stagnation flow reactor
    - 500 W CW NIR laser heating
    - Modulated beam mass spectrometer
- Screen for O_2 uptake and release.
  - Assess redox viability
- 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











- **Assess material behavior at heating rates > 10°C/s.**
- **Expose material to many rapid heating cycles.**

Packed Particle Bed Reactor Design and Operation

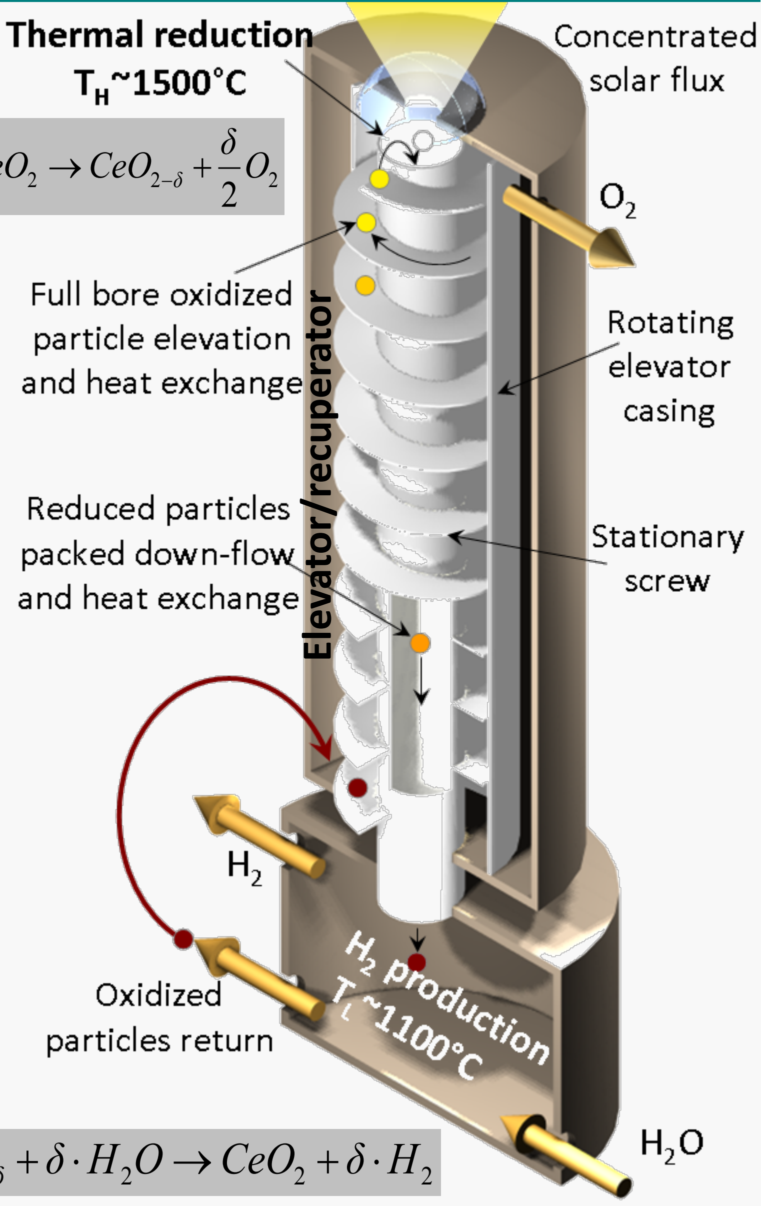
Key efficiency attributes:

- **DIRECT solar absorption by working material (>90%).**
- **EFFICIENT heat recovery between T_H & T_L (>75%).**
- **CONTINUOUS on-sun operation.**
- **INTRINSIC gas and pressure separation (H_2 from O_2).**

Specific design advantages:

- Small reactive particles (~100μm)
- Only particles are thermally cycled
- Only one high T moving part: a ceramic tube
- Independent component optimization
- Straightforward material replacement
- Uses established high T and vacuum techniques [Cement kiln: 1450°C; LPCVD: <150 Pa]

- **High performance particle receiver reactor embodies ALL key efficiency attributes.**

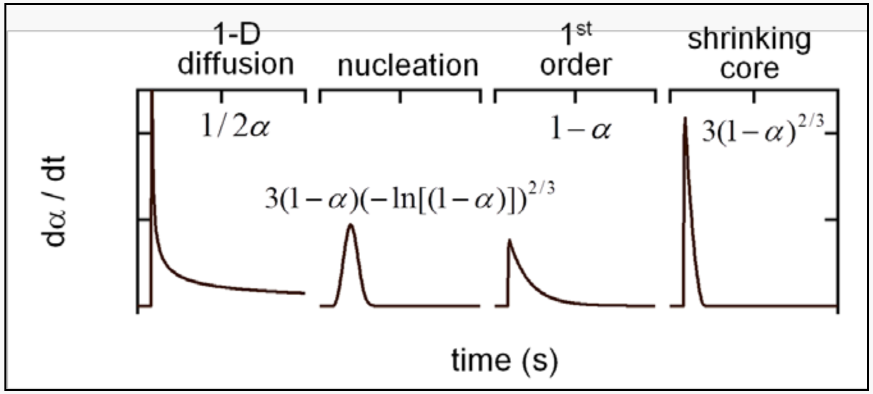


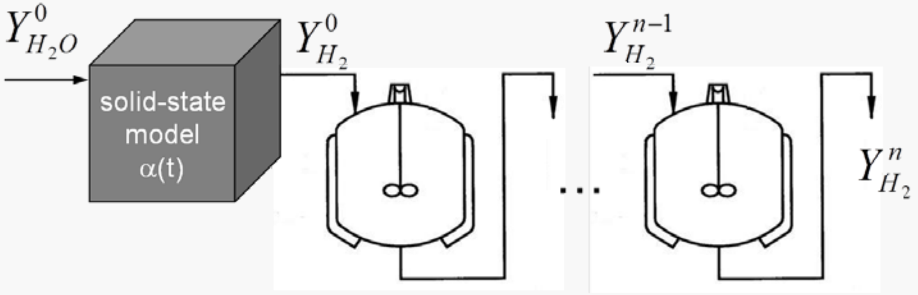
$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2$$

U.S. Patent Filed, 2011

Developed Model-based Data Reduction Protocol





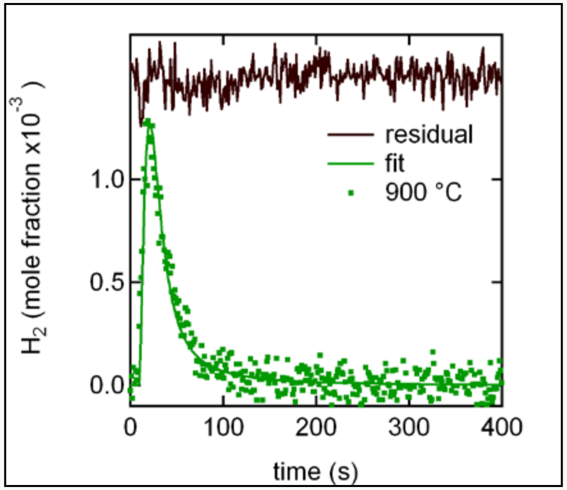
$$\frac{d\alpha}{dt} = k[Y^0_{H_2O}(t-t_{shift})]^\gamma \exp[-E/RT]\cdot f(\alpha)$$

$$Y^0_{H_2} \propto \frac{d\alpha}{dt}$$

$$\frac{dY^n_{H_2}}{dt} = \tau\cdot(Y^{n-1}_{H_2} - Y^n_{H_2})$$

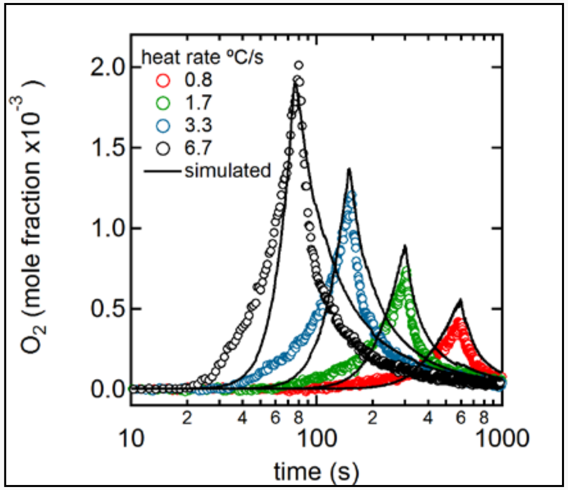
- Solid state kinetic theory.
  - Use 14 validated expressions for $f(\alpha)$
  - Resolve rate-governing mechanism
- Numerical procedure.
  - Coding is Mathematica® based
    - Stiff integrators
    - Global least squares optimization
  - Correct experimental artifacts

- **Analytical approach new to this field of research.**
- **Generate high fidelity predictions of kinetic behavior.**
- **Establish and test performance metrics.**
  - Both materials and reactor design



Developed Validated Kinetic Model for $CeO_{2-\delta}$ Redox

thermal reduction at 1500 °C

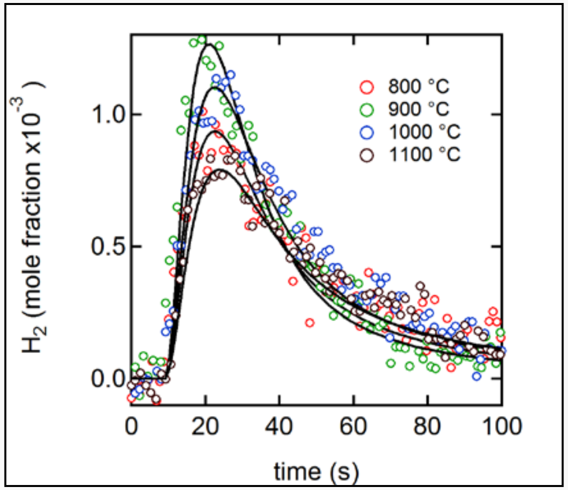


$$\frac{d\delta}{dt} = k_1\left(\frac{T}{T_1}\right)^{\beta_1} \exp\left[-E_1/RT\right]\cdot(\delta_{eq}-\delta)^{m_1}$$

- Reduction kinetics very rapid.
  - Solid-state dynamics at *mm length scales* does not limit kinetics

- **CeO_2 is a good model material.**
- **Use to evaluate reactor performance metrics.**
  - Mass flow, reactor geometry
  - Reaction time and temperature

H_2O oxidation



$$\frac{dY^0_{H_2}}{dt} \propto \frac{d\alpha}{dt} = k_2\left[Y^0_{H_2O}(t-t_{shift})\right]^{\gamma} \exp\left[-E_2/RT\right]\cdot(1-\alpha)^2$$

- H_2 production rate exhibits 2nd order behavior.
- 90% conversion in 100 s @ 900°C.
  - 10- 100 μm size particles

property	ceria (CeO_2)	ideal
redox kinetics	**FAST**	**FAST**
durability	**HIGH**	**HIGH**

Synthesized and Characterized Doped Ceria Materials

ferrites		ceria	perovskites	
Fe_2O_3	$CoFe_2O_4$	$MO_x:CeO_{2-\delta}$	$La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$	
YSZ m-ZrO_2	m-ZrO_2	10 mol% Mn, Ni, Co, Mo, & Fe	X 0.9 0.8 0.7 0.6 0.5	Y 0.5
CeO_2				
Al_2O_3	Al_2O_3			

- Current material chemistries under consideration.
  - Chemical systems
    - $M^{+n}/M^{+(n+1)}$ redox couples
    - $MO_{n-\delta}$ non-stoichiometric oxides
    - CU “hercynite”
  - Supports
    - m-ZrO_2, YSZ, CeO_2, Al_2O_3

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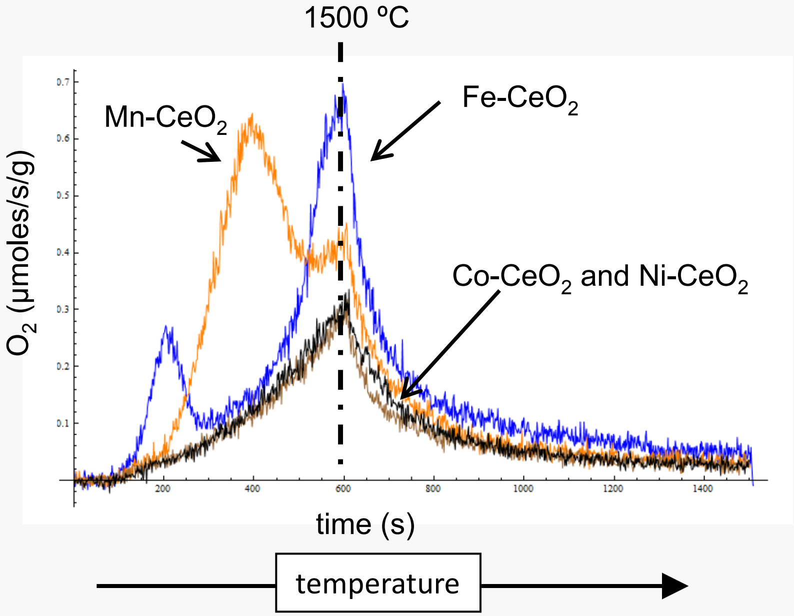
property	ceria (CeO_2)	ideal
redox capacity	LOW	HIGH
reduction T_H	HIGH	LOW

- **Destabilized CeO_2 more likely to achieve DOE performance targets.**

- **Improve material performance through chemical modification.**
  - Create solid solutions with transition metals
- **Increase oxygen non-stoichiometry (redox capacity).**
- **Decrease thermal reduction temperature (T_H).**

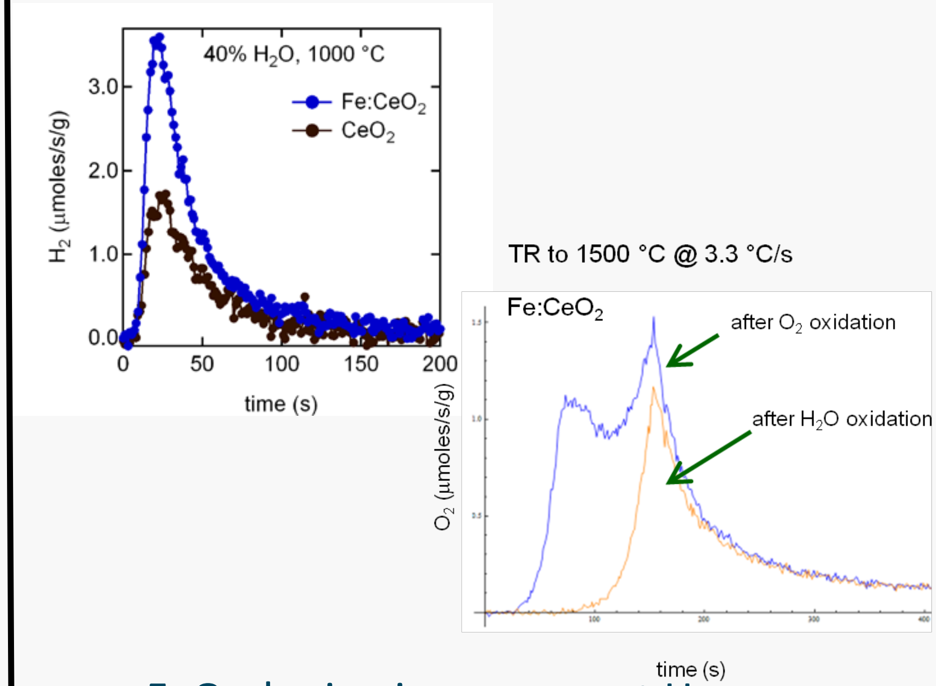
Characterized Effects of Transition Metal Doping on $CeO_{2-\delta}$

thermal reduction at 1500°C



- O_2 evolution complex for Mn and Fe.
  - More O_2 evolved per unit mass of material than undoped CeO_2
  - Multiple valence states for Mn and Fe cations likely in doped system
- O_2 evolution unchanged for Co and Ni.

H_2O oxidation

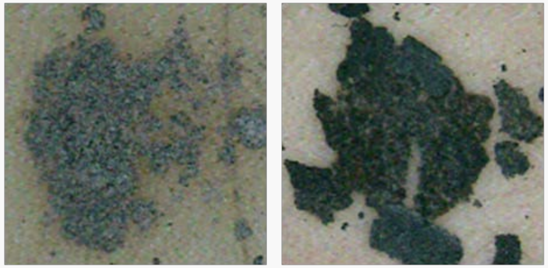


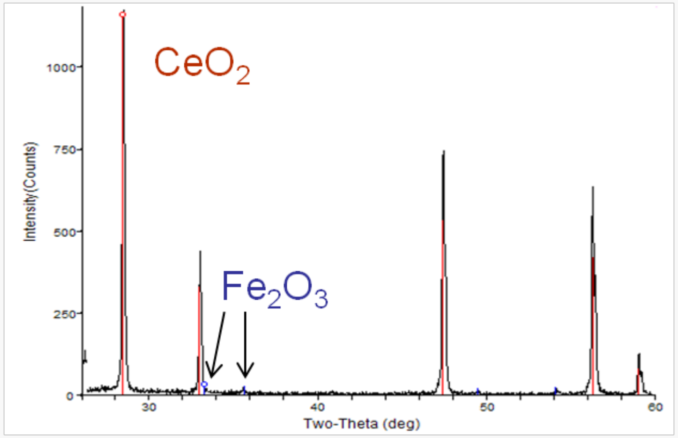
- FeO_x doping increases net H_2 production.
- Active sites in Fe-doped CeO_2 oxidize at different rates.

- **Fe and Mn change CeO_2 material behavior.**
  - More O_2 evolves at lower temperature (increase capacity at lower T_H)
- **Difficult to re-oxidize added capacity by water splitting chemistry.**

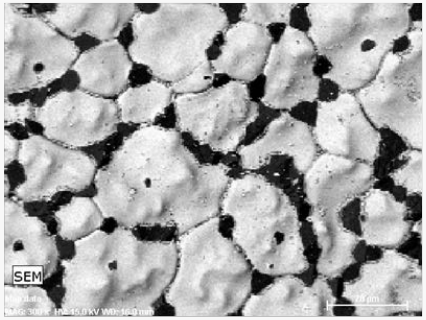
Iron Doping Induces Morphological Instability

before redox after redox

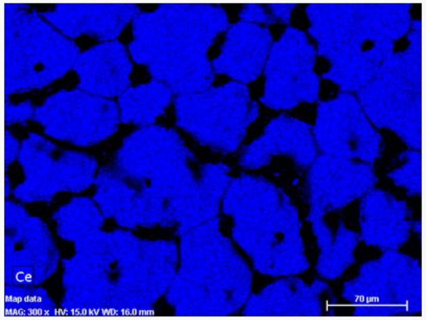




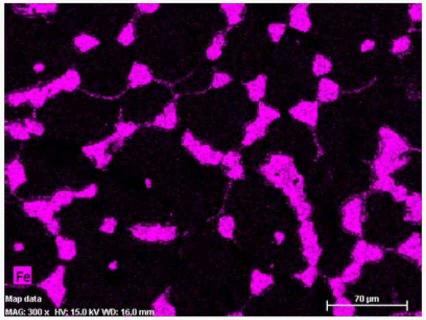
SEM image



Ce = BLUE



Fe = PINK



- Reduction in helium at 1500°C followed by H_2O oxidation at 1000°C.
  - Severe problems with sintering and reactivity with other ceramics
  - Fe phase segregation evident in SEM-EDS despite lack of evidence in XRD
  - Slow kinetics on “low temperature” O-site

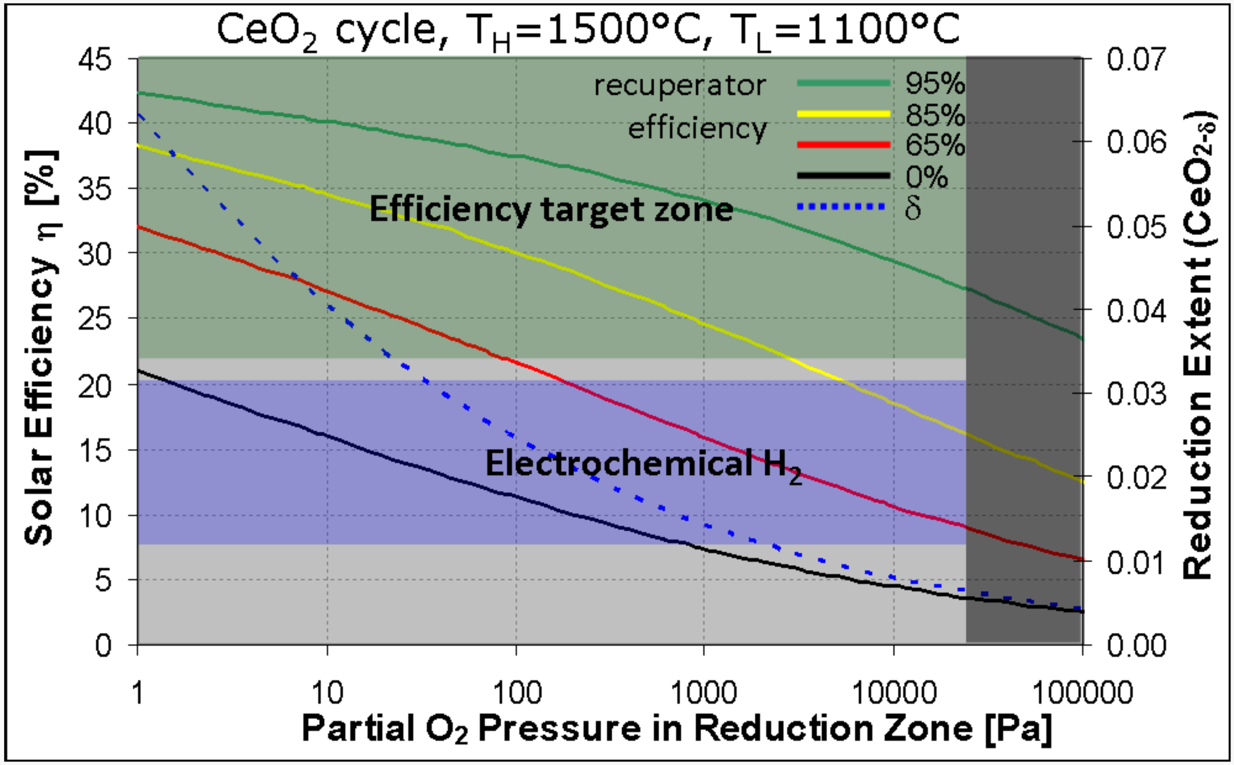
- **Fe doping not likely a viable strategy despite greater redox capacity.**
  - Other doping strategies may work!

Theoretical Analysis of Sandia Reactor Concept: Solar-to-H_2 Efficiency

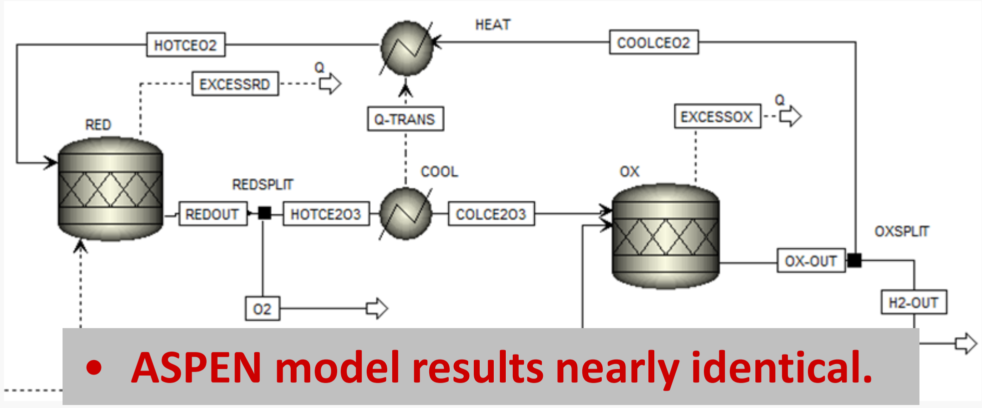
All-inclusive efficiency metric:

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

$$\eta = \frac{\dot{n}_{H_2} \cdot HHV_{H_2}}{P_S}$$

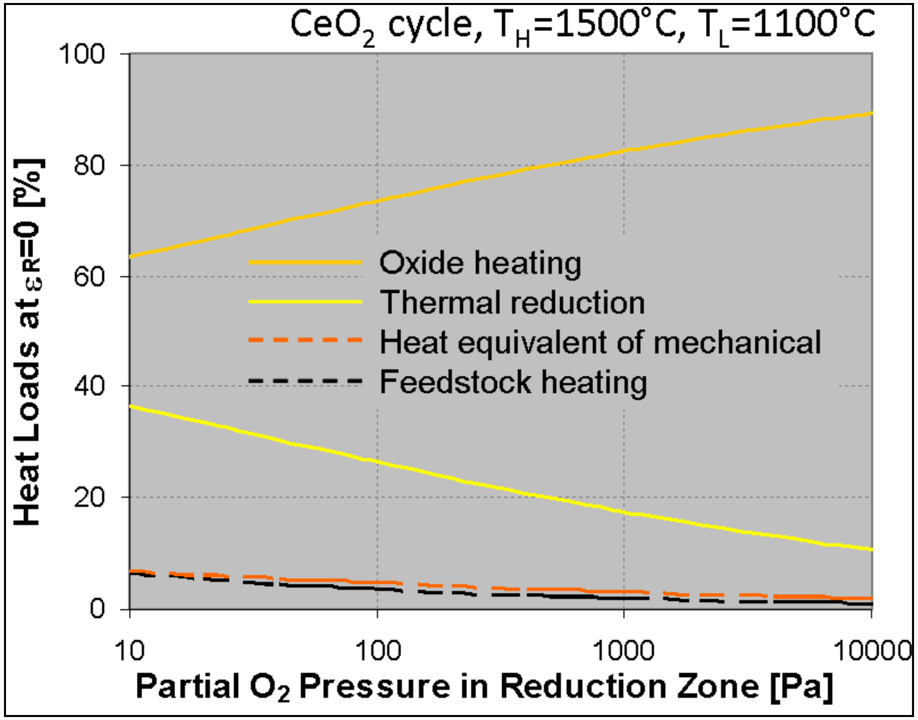


- **Theoretical Solar-to-H_2 efficiency >30% possible with CeO_2.**
- **Must haves:**
  - Heat recovery (recuperation)
  - Low O_2 pressure in reduction zone

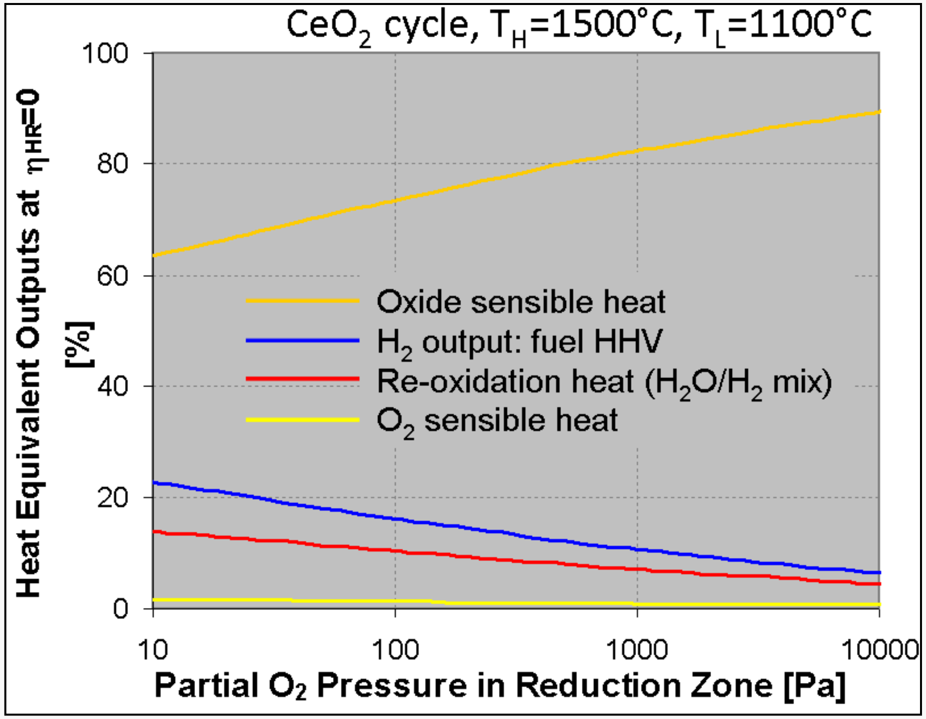


- **ASPEN model results nearly identical.**

Heat Recuperator Effectiveness Critically Important



- Oxide heating and reduction.
  - Must be driven by direct solar input
- Other loads can use waste heat.



- Heat (or equivalents) of reactor output.

- **Heat recovery critical to efficient system operation.**
- **Recuperator effectiveness >65% required to meet DOE performance goals.**

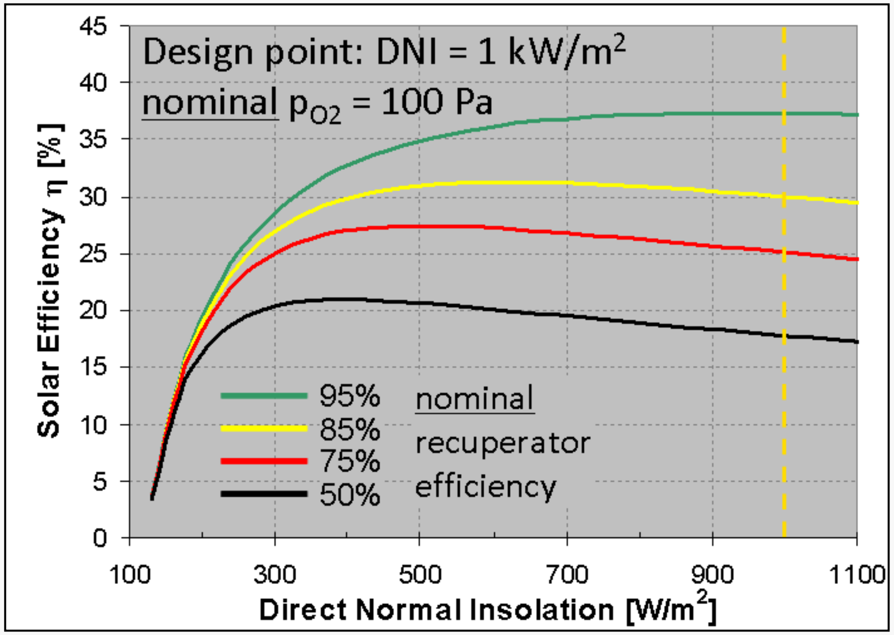
Achieving Effective Heat Recuperation in a Particle Elevator

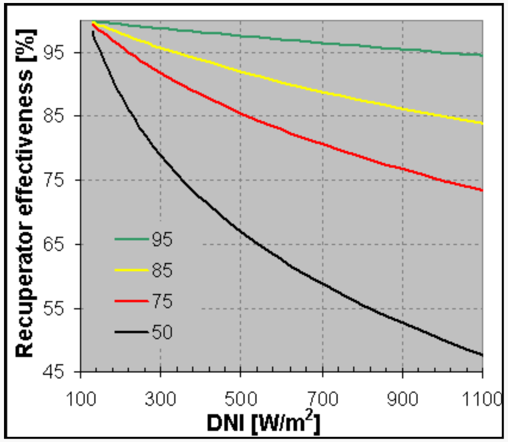
- Innovative reactor design (Sandia patented).
  - Stationary screw with rotating casing
- Internal fins used for enhanced heat recovery.
- Use multiple screw design to increase heat recovery.
  - Single standard-pitch elevator screw inefficient

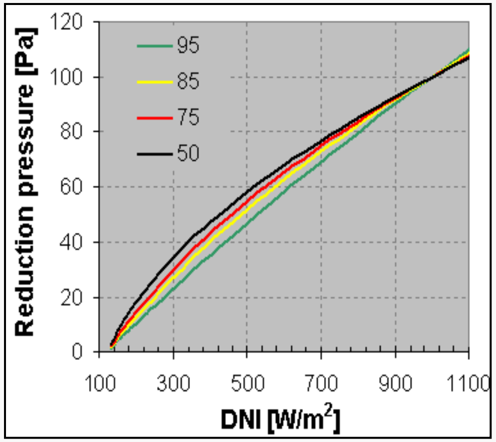
- **Nested multi-screw design is most promising elevator/recuperator concept we have tested to date.**
  - Move 30 g/s particles at 20 RPM
- **Building prototypes to assess heat recuperation effectiveness.**

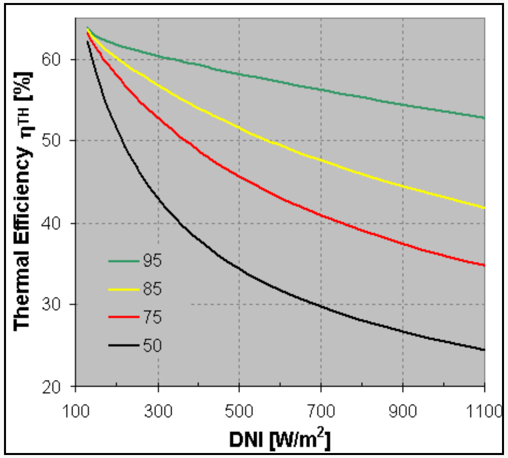
Collaboration with Jenike & Johanson Inc.

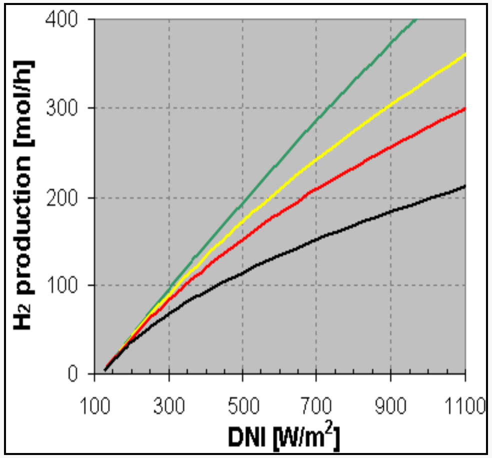
Sandia Reactor Also Operates Efficiently at Low DNI



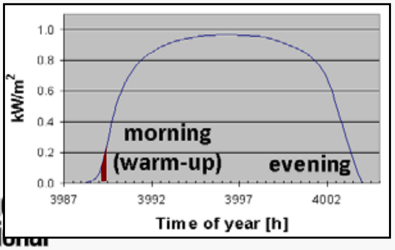








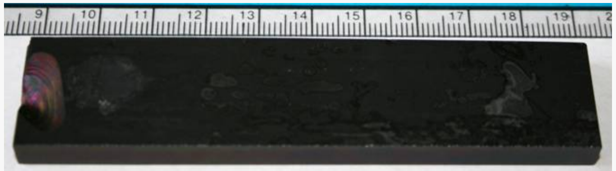
Low DNI → Increased heat recovery & Decreased p_{O2} → High efficiency



- **High solar utilization under most operating conditions.**
  - 25% solar-to-H_2 annual average efficiency expected
- **Use low DNI in the morning for system warm-up.**

Materials Compatibility and Manufacturing

- Reactor parts and reactive oxide must not react with each other, even at T_H.
- Multiple bare and coated materials tested under realistic conditions.
- Alumina compatible with ceria to at least 1550°C.
- SiC compatible with ceria to 1400°C.
- Alumina-coated SiC compatible to 1450°C (coating thickness, method, and stability critical).
- Ceramic component manufacturers identified.



CeO_2/SiC Hexoloy, 1400°C
stagnant air, 3h

CeO_2/Al_2O_3, 1550°C
stagnant air, 3h

paint CeO_2/Al_2O_3/SiC, 1450°C
stagnant air, 3h

- **For a ceria reactive oxide, no showstoppers in prototype manufacture are expected.**

Collaborations

- Currently working with Prof. Alan Weimer’s group at the University of Colorado.
  - Several students are working at SNL/CA in the area of materials discovery and characterization
- Currently working with Prof. Nathan Siegel at Bucknell University.
  - Optics, particle conveyance, systems and economic analysis
- Jenike and Johanson Inc. contracted to help develop particle conveyor concepts.

Proposed Future Work

- Find perovskite materials that exhibit low thermal reduction temperature, fast exchange kinetics, and increased redox capacity.
  - Synthesize novel, substituted ABO_3 perovskites
    - Future collaboration with Colorado School of Mines
    - Future collaboration with North Western University via an NNSA fellow
  - Develop a method to use simple thermodynamic assessments to guide search
    - Use structure-property and structure-performance relationships as descriptors
- Build a reactor prototype platform to test various functionalities at increasing temperatures (<200°C, ~900°C, ~1500°C). Target power ~5 kWthermal
  - Develop a manufacturing process for CeO_2
    - Correctly-sized particles and quantities (~100 kg needed for 5kW)
  - Evaluate particle flow and attrition as a function of particle and elevator dimensions
  - Evaluate steam flow through particle bed in the H_2 production chamber
  - Measure particle bed permeability and gas flow between reactor chambers
  - Test reactor performance in a solar furnace or solar simulator (T > 1400°C)
- Systems analysis.
  - Critically evaluate central receiver performance
  - Detailed annual average performance analysis

Summary

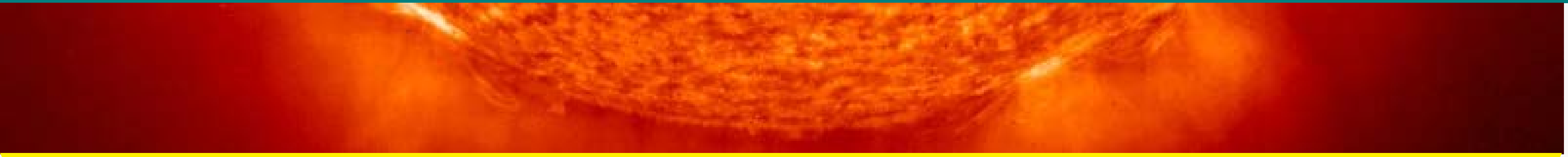
- Developed a novel analytical approach to characterizing reactive materials.
  - Used to generate high fidelity predictions of CeO_2 kinetic behavior
  - Used to establish and test performance metrics for both reactor designs and materials
- Synthesized and characterized the redox behavior of several transition-metal doped CeO_2 compounds (Mn, Fe, Co, Ni, and Mo).
  - Chemical modification of CeO_2 may improve material performance
- Designed and theoretically analyzed new solar thermochemical reactor that embodies four key high-efficiency attributes: direct solar absorption, efficient heat recovery, continuous on-sun operation, and intrinsic gas and pressure separation.
  - Design can attain a solar-to-H_2 conversion efficiency >30%
  - Determined that heat recovery (recuperation >65%) critical for efficient performance
  - Determined that efficient operation possible even in low DNI

    25% solar-to-H_2 annual average efficiency expected
- Prototyped a novel particle elevator/recuperator reactor concept.
  - Particle conveying experimentally validated using a unique nested-screw design
  - U.S. patent filed in 2011

Technical Backup

Technical Back-Up Slides

System Level: Many Losses and High Annual Efficiency



Resource efficiency = 95% for Daggett, CA (DNI > 300W/m^2)

Operational ~ 94%

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

Optical ~ 79%

Reflectivity = 93% (two reflections)

Dirt = 95%

Window = 95%

Tracking = 99%

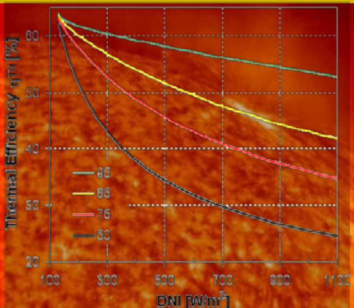
Intercept = 95%

Receiver ~ 82%

Radiation = 82%

Conduction/Convection = 0 %

Solar-to heat: ~58% → **Thermal ~44%**



→ **~25% solar to H_2 annual average**

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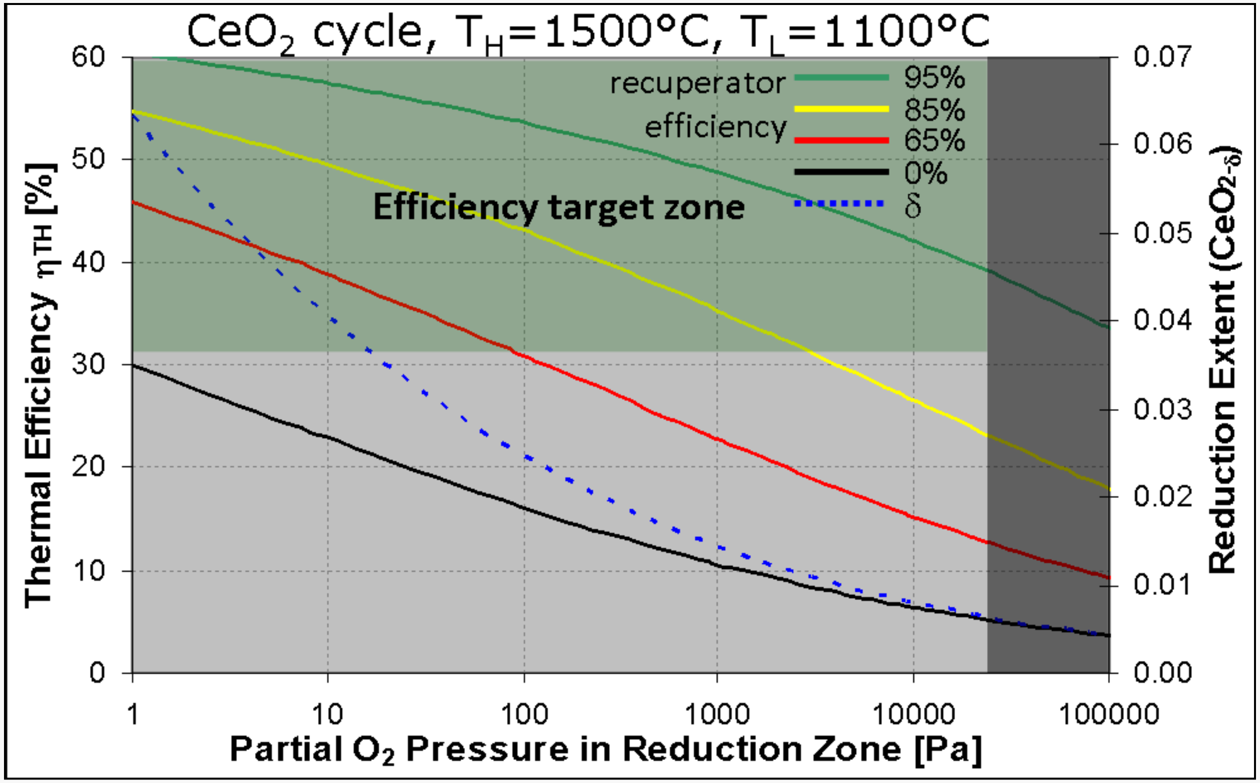
Reactor Performance Model: Thermal Efficiency

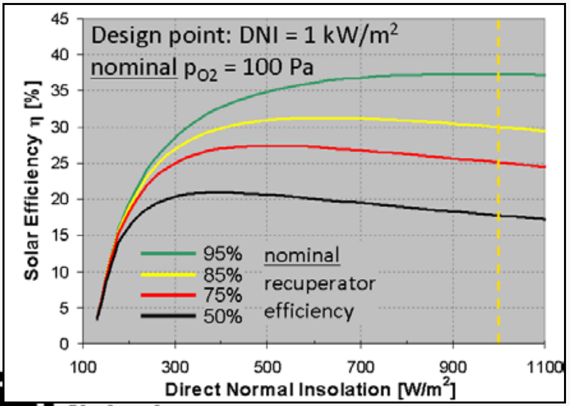
Reactor-only metric includes:

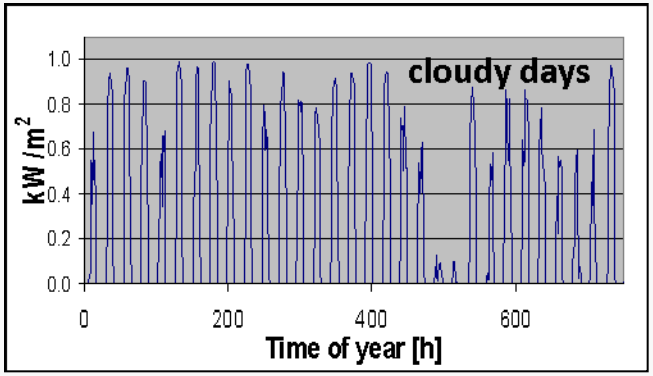
- Oxide heating.
- Oxide thermal reduction.
- Feedstock heating (steam).
- Pumping.
- Electrical/mechanical.

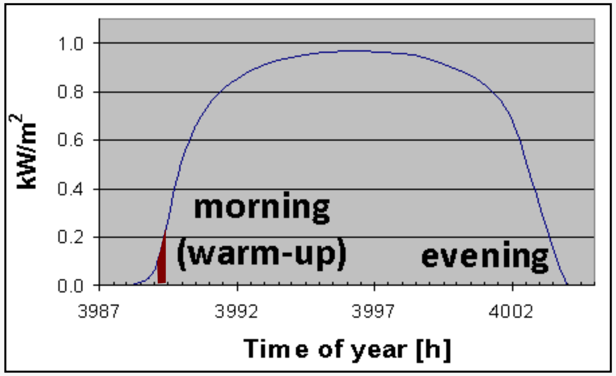
$$\eta = \frac{\dot{n}_{H_2} \cdot HHV_{H_2}}{P_{TH}}$$

- **Thermal efficiency >40% attainable.**
- **Excellent low-DNI efficiency**

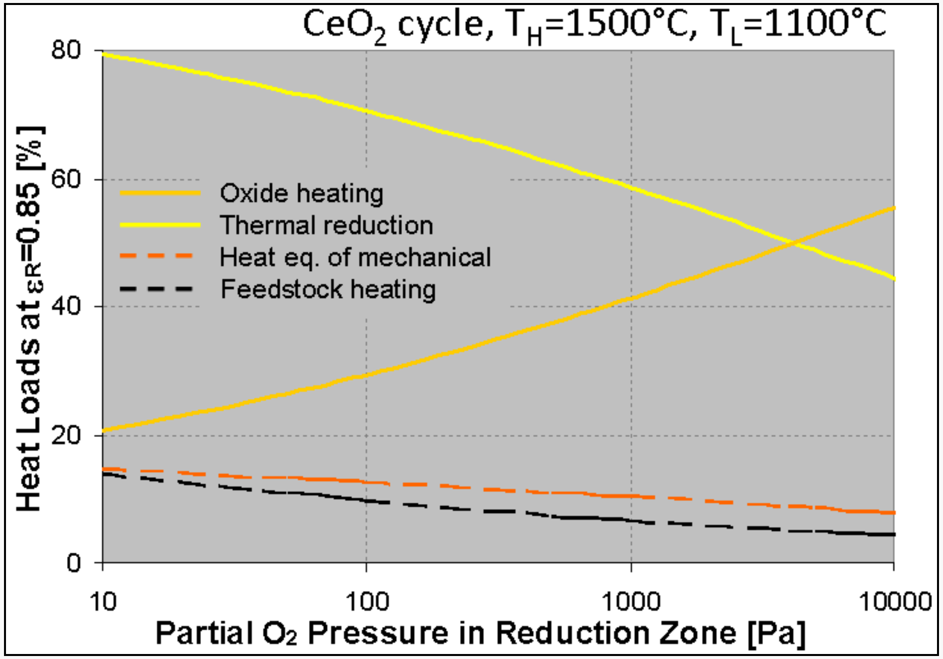


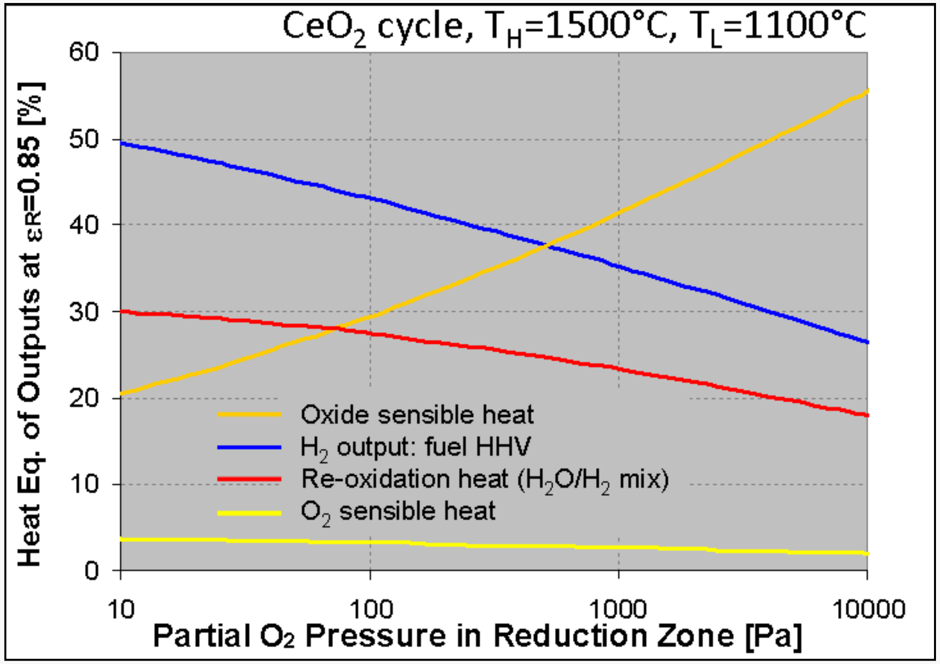






Heat Recuperator Effectiveness Critically Important



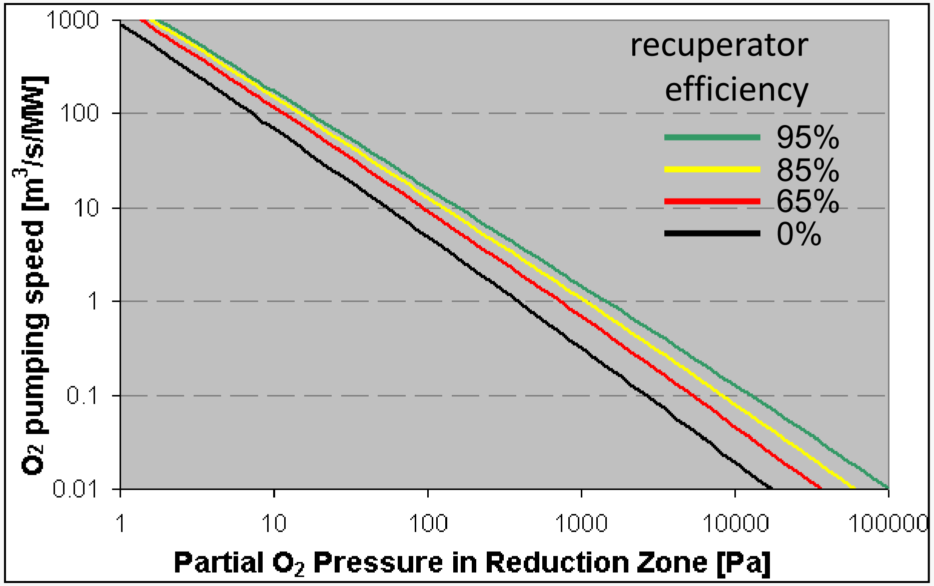


- Oxide heating and reduction.
  - Must be driven by direct solar input
- Other loads use waste heat.

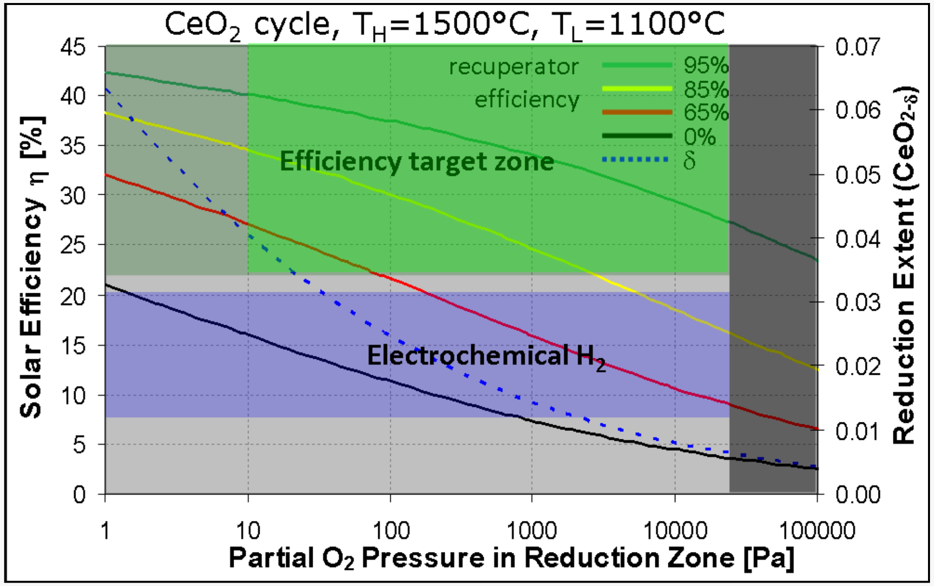
- Heat (or equivalents) of reactor output.

- **Heat recovery critical to efficient system operation.**
- **Recuperator effectiveness >65% required to meet DOE performance goals.**

Low Pressure Limit: Pumping Speed



Required pumping speed for 1 MW_{solar} device



- **Pumping speed requirement is a likely limit to minimum design-point p_{O2} or maximum solar power input per device.**