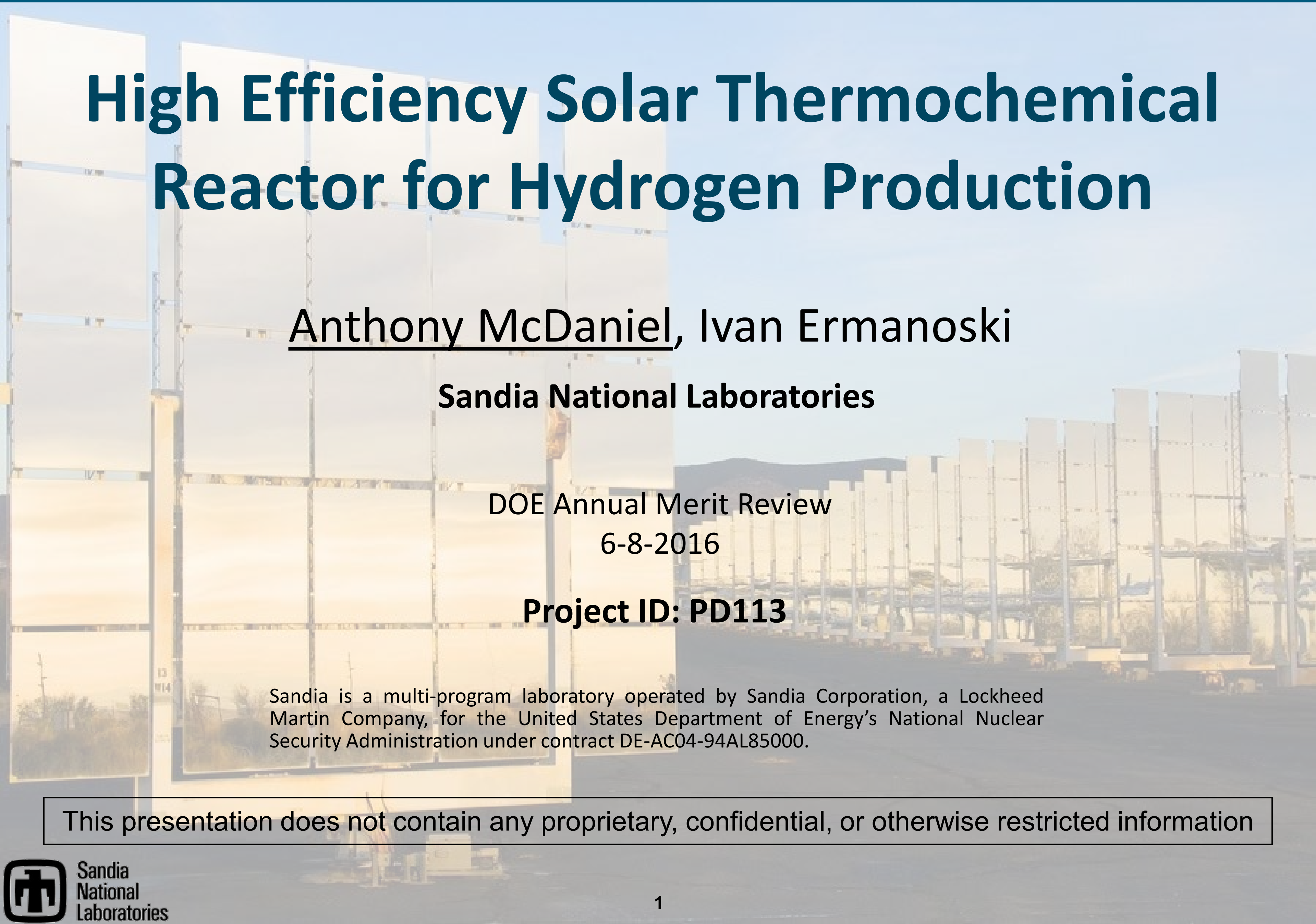


High Efficiency Solar Thermochemical Reactor for Hydrogen Production

Anthony McDaniel, Ivan Ermanoski

Sandia National Laboratories

DOE Annual Merit Review
6-8-2016

Project ID: PD113

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: 10/01/2014
- Project End Date: 12/31/2016
- Project Complete: 65%

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.
  - $3.293M
- Total Recipient Share.
  - $0.243M
- Total Federal Share.
  - $3.050M
- Total DOE Funds Spent:*
  - $1.849M

Partners

- German Aerospace Center-DLR , Cologne DE.
  -Dr. Christian Sattler
- Arizona State University, Tempe AZ.
  -Profs. Ellen Stechel and Nathan Johnson
- Bucknell University, Lewisburg PA.
  -Prof. Nathan Siegel
- Colorado School of Mines, Golden CO.
  -Profs. Ryan O'Hayre and Michael Sanders
- Northwestern University, Evanston IL.
  -Prof. Christopher Wolverton
- Stanford University, Stanford CA.
  -Prof. William Chueh

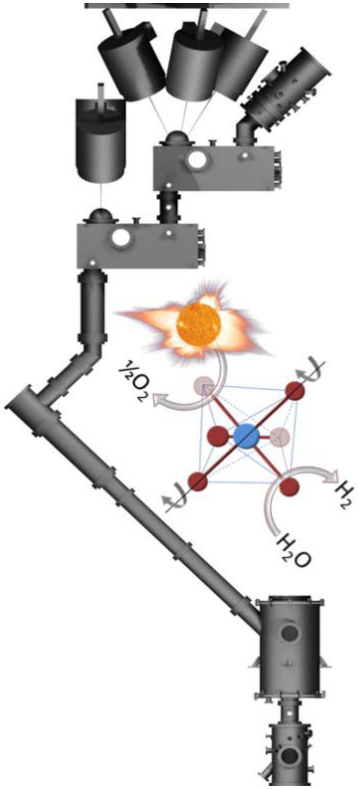
*As of 03/31/16

Relevance

- **DOE Objective: 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 and validate a particle bed reactor for producing hydrogen via a thermochemical water-splitting cycle using a non-volatile metal oxide as the working fluid. Demonstrate 8 continuous hours of "on-sun" operation producing greater than 3 liters of H_2.**

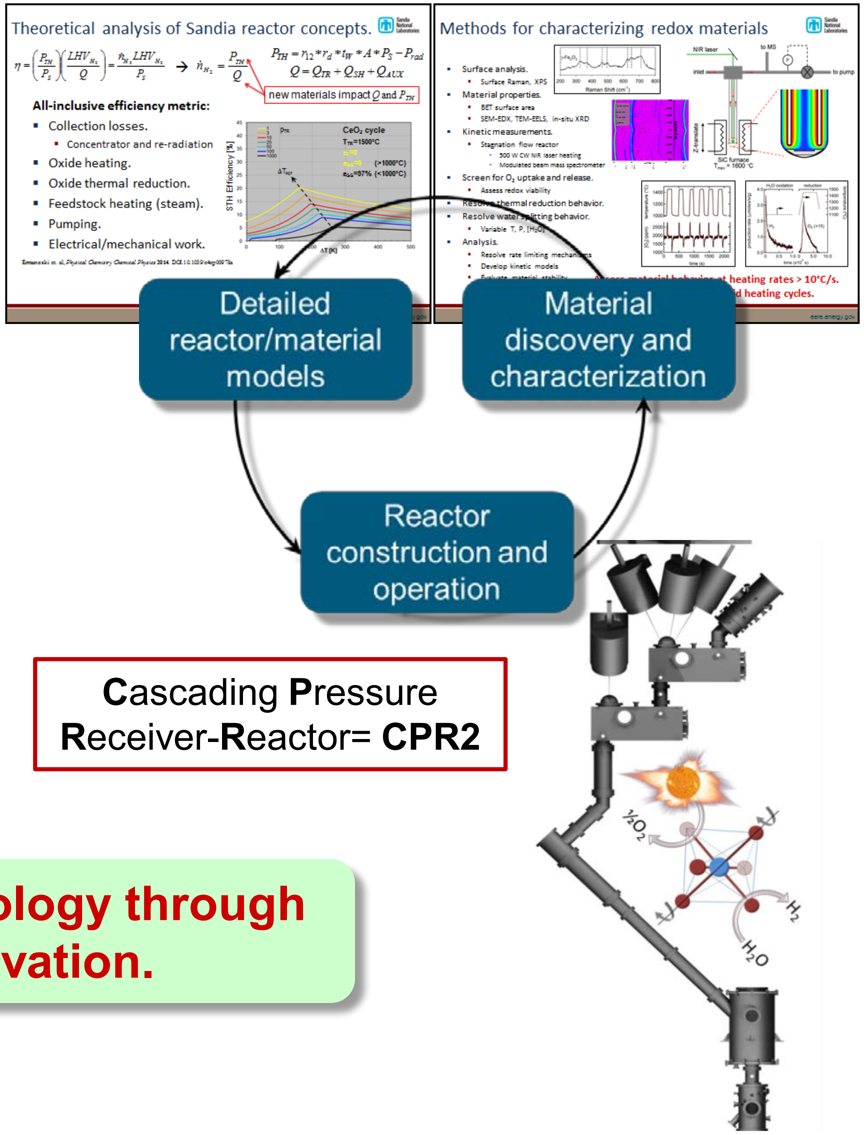
- **FY 2016 Objectives:**
  - Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. (**Barrier S & T**)
  - Construct and demonstrate a particle receiver-reactor capable of continuous operation at 3kW thermal input. (**Barrier T**)
  - Conduct full technoeconomic, sensitivity, and trade-off analysis of large-scale H_2 production facility using a plant-specific predictor model coupled to H2A . (**Barrier X**)



Approach

Reactor and Materials Innovation

- **Overcoming barriers to high-temperature solar thermochemical H_2 production.**
  - Novel cascading pressure design achieves very low O_2 pressures during reduction
  - Novel material formulations (perovskites, others) for lower reduction temperature
  - Maximize STH efficiency by exploiting reactor-material synergies
  - Reduce dependence on high-temperature solid-solid heat recovery by 50%



Theoretical analysis of Sandia reactor concepts.

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

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

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

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.

Ermanoski et. al, *Physical Chemistry Chemical Physics* 2014. DOI:10.1039/c4cp00978a

Methods for characterizing redox materials

- Surface analysis.
  - Surface Raman, XPS
- Material properties.
  - BET surface area
  - SEM-EDX, TEM-EELS, in-situ 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

Assess material behavior at heating rates > 10°C/s.

d heating cycles.

Detailed reactor/material models

Material discovery and characterization

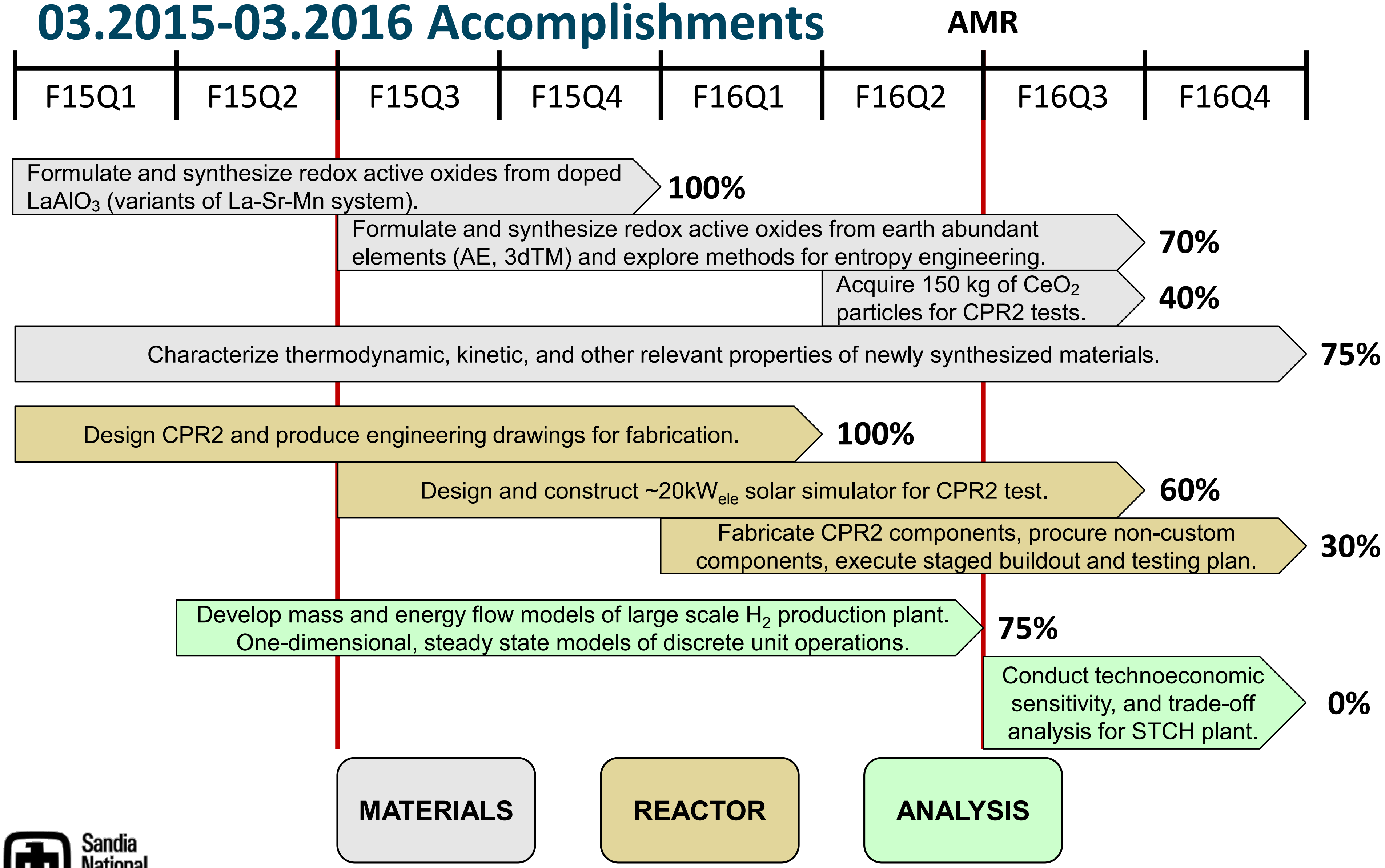
Reactor construction and operation

Cascading Pressure Receiver-Reactor= **CPR2**

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

Progress Metrics

03.2015-03.2016 Accomplishments



Formulate and synthesize redox active oxides from doped $LaAlO_3$ (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. **70%**

Acquire 150 kg of CeO_2 particles for CPR2 tests. **40%**

Characterize thermodynamic, kinetic, and other relevant properties of newly synthesized materials. **75%**

Design CPR2 and produce engineering drawings for fabrication. **100%**

Design and construct ~20kW$_{ele}$ solar simulator for CPR2 test. **60%**

Fabricate CPR2 components, procure non-custom components, execute staged buildout and testing plan. **30%**

Develop mass and energy flow models of large scale H_2 production plant. One-dimensional, steady state models of discrete unit operations. **75%**

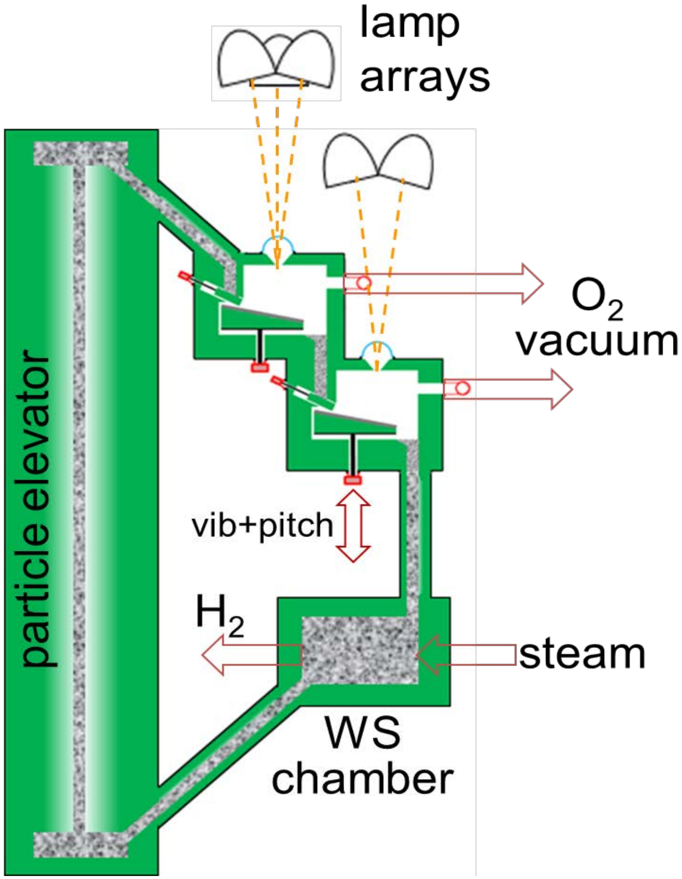
Conduct technoeconomic sensitivity, and trade-off analysis for STCH plant. **0%**

MATERIALS

REACTOR

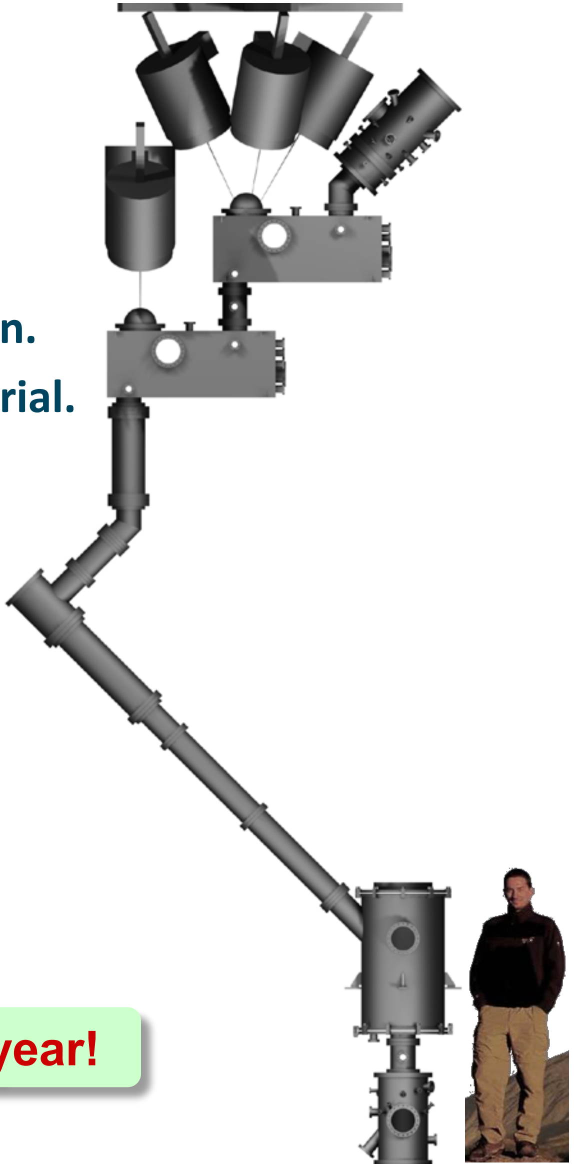
ANALYSIS

Cascading Pressure Receiver-Reactor (CPR2)



CPR2 design specifications:

- Fully instrumented.
- $20kW_{ele}$ solar simulator.
- T_{TR}=1500 °C, T_{WS}=800 °C.
- 1700× pressure separation.
- 100 kg redox-active material.
- 2.5 g/s particle flow rate.
- 0.3 slpm H_2 continuous.

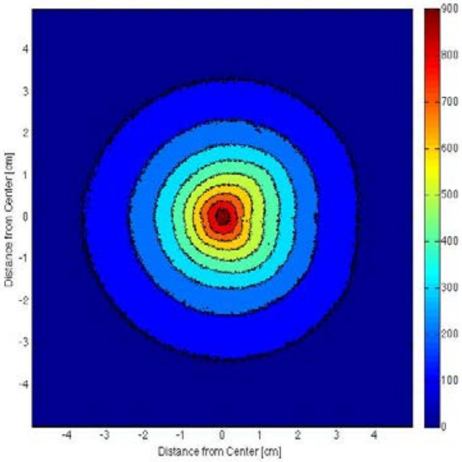


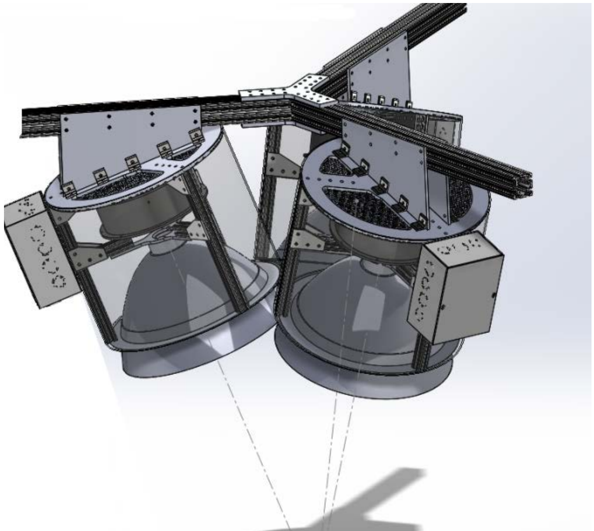
- From concept to fabrication in 1 year!

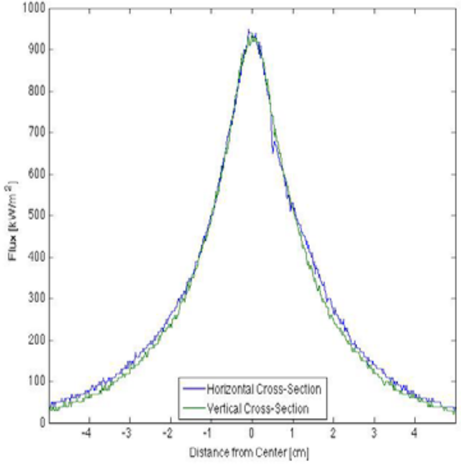
20kW$_{ele}$ Solar Simulator to Power CPR2

- **Designed in collaboration with Bucknell University.**
- **Each module houses a 2.5kW short-arc Xe bulb.**
- **Each module independently focused into the CPR2 receiver aperture.**

- **Design validated by flux mapping combined with ray tracing calculations.**

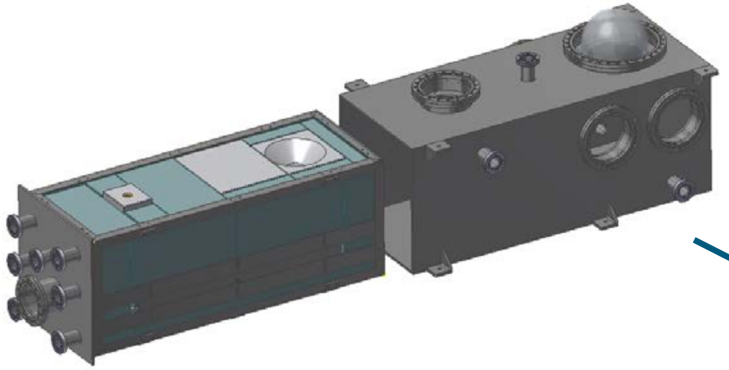


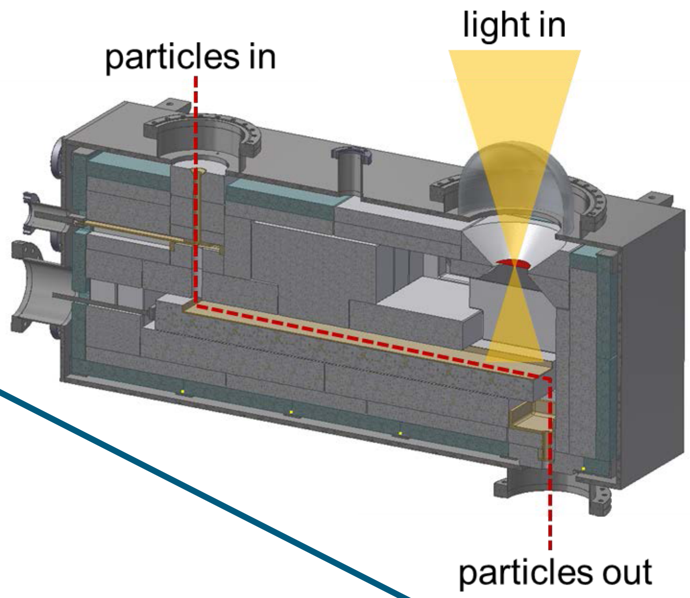




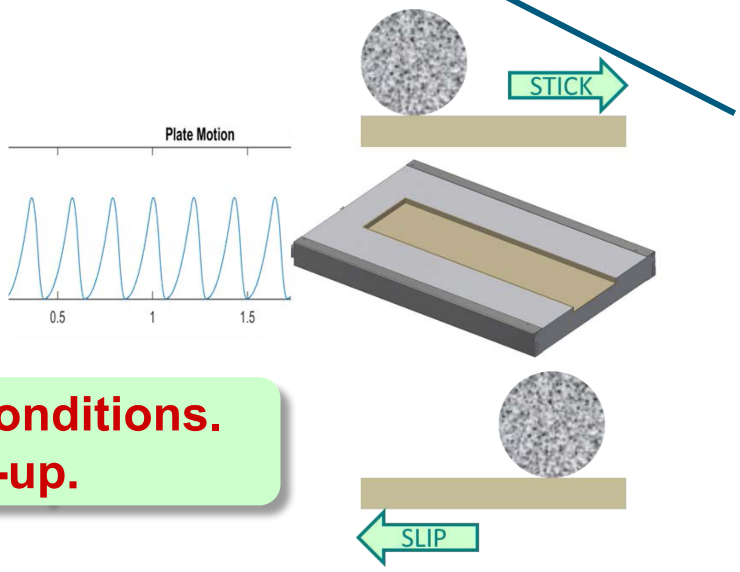
- **Provide 7kW$_{th}$ of simulated concentrated solar power into the CPR2.**

Ultra-high Temperature Solar Receiver-Reactor



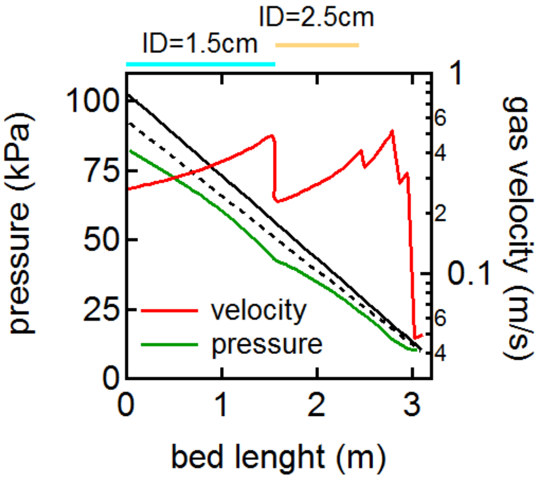


- **Designed in collaboration with DLR and Bucknell University.**
  - High vacuum, P_{TR}=.0005 atm
  - Radiant cavity, T_{wall}=1500 °C
  - Direct illumination of particles
  - Control particle flow rate and particle irradiation time
- **Design validated by numerical models, ray tracing, particle flow tests, etc...**



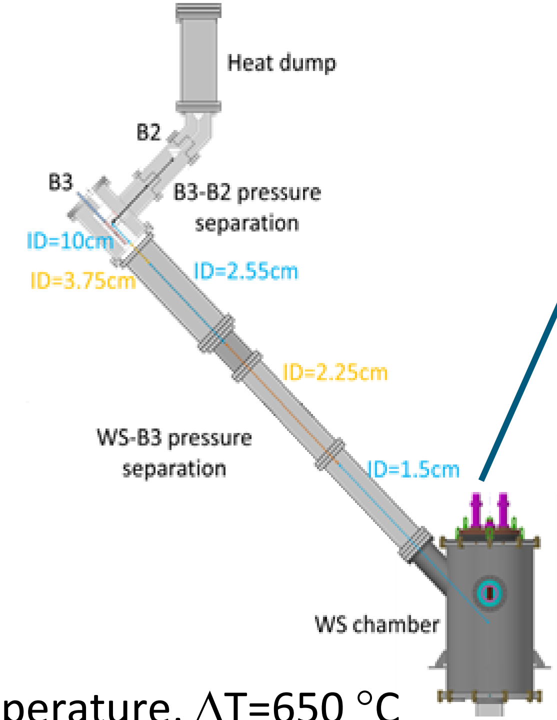
- **Precise control of oxide reduction conditions.**
- **Generate engineering data for scale-up.**

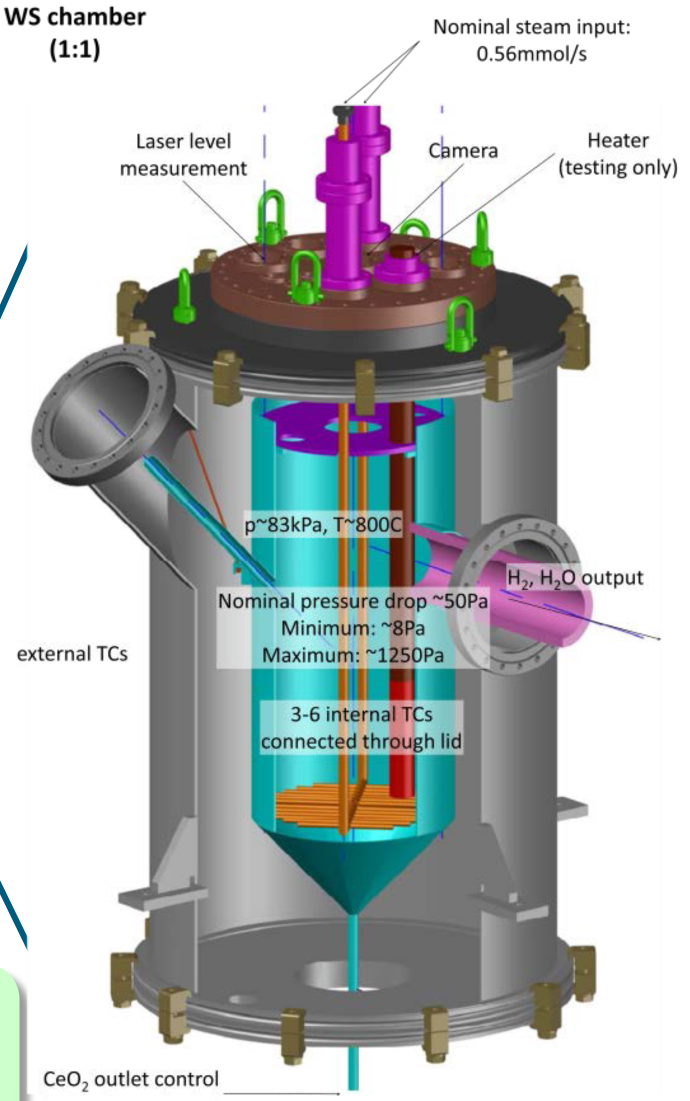
Pressure Separation and Water Splitting Chamber



1700× pressure reduction without fluidization of moving particle bed

- **Designed by Sandia.**
  - Quench particle temperature, ΔT=650 °C
  - Stand off 0.84 atm pressure
  - Separate O_2 from H_2
  - Long contact time between H_2O and oxide

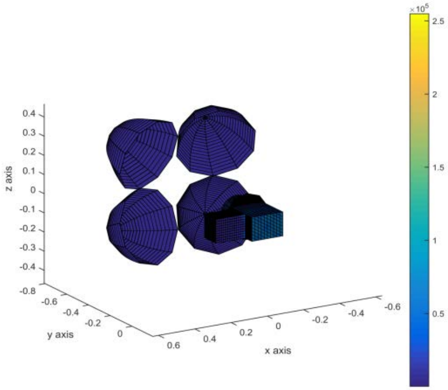


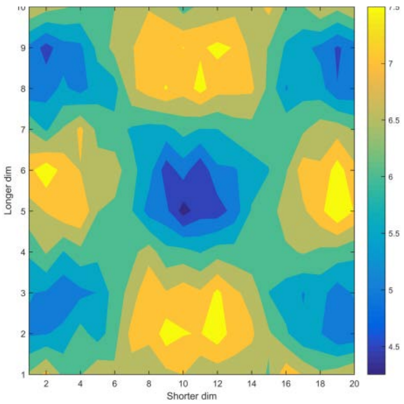


- **Demonstrate increased H_2 production efficiency with pressure separation and countercurrent flow between H_2O and oxide.**

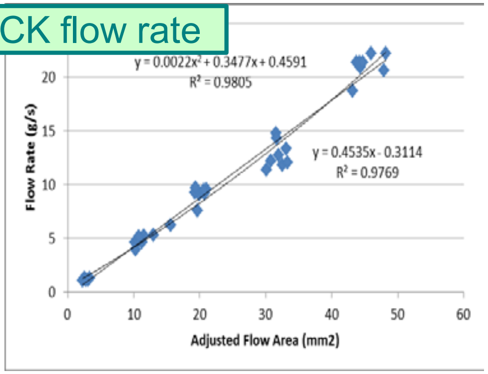
Selected Design Validation Activities

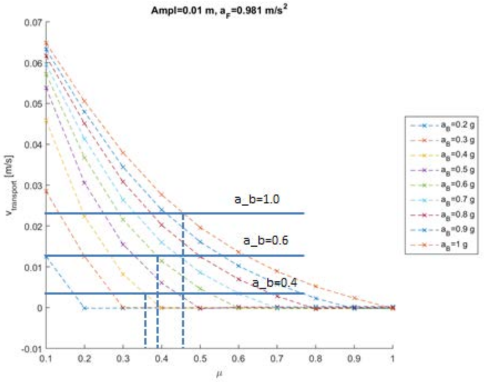
calculate flux on particles



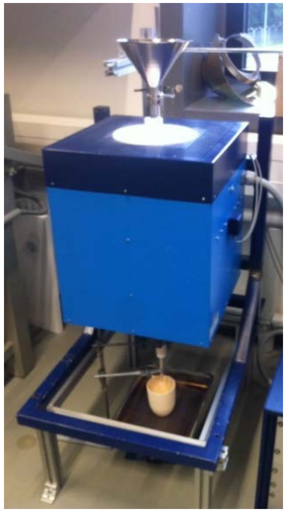


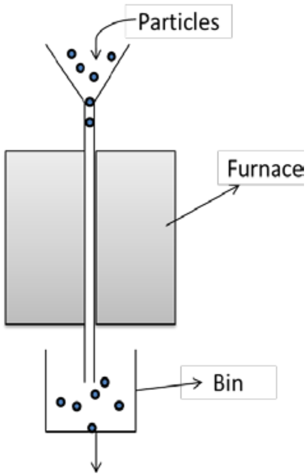
calibrate SLIP-STICK flow rate



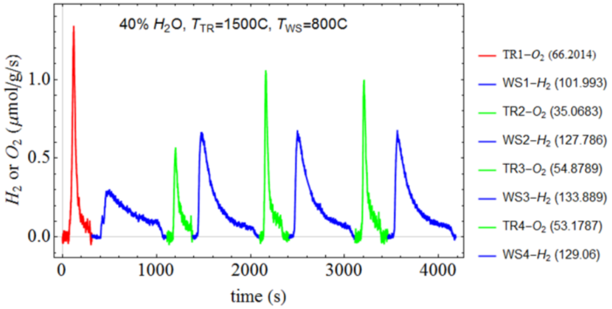


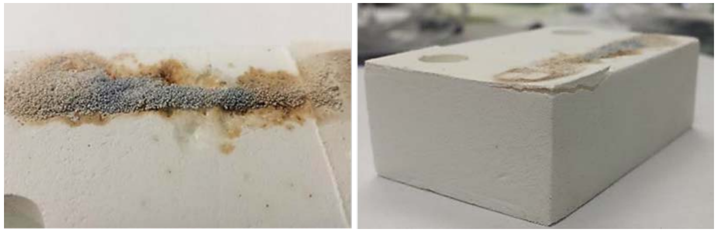
evaluate particle flow at high T





test chemical & thermal stress on materials





- **Qualify design choices to mitigate risk of CPR2 failure.**

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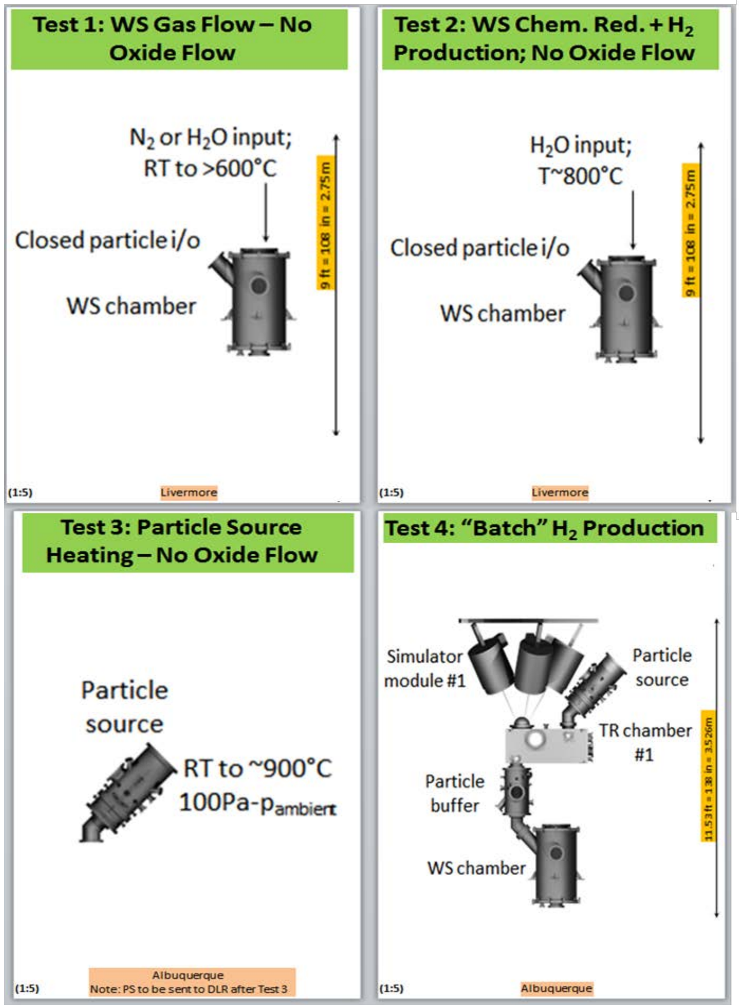
Aggressive Assembly and Demonstration Schedule



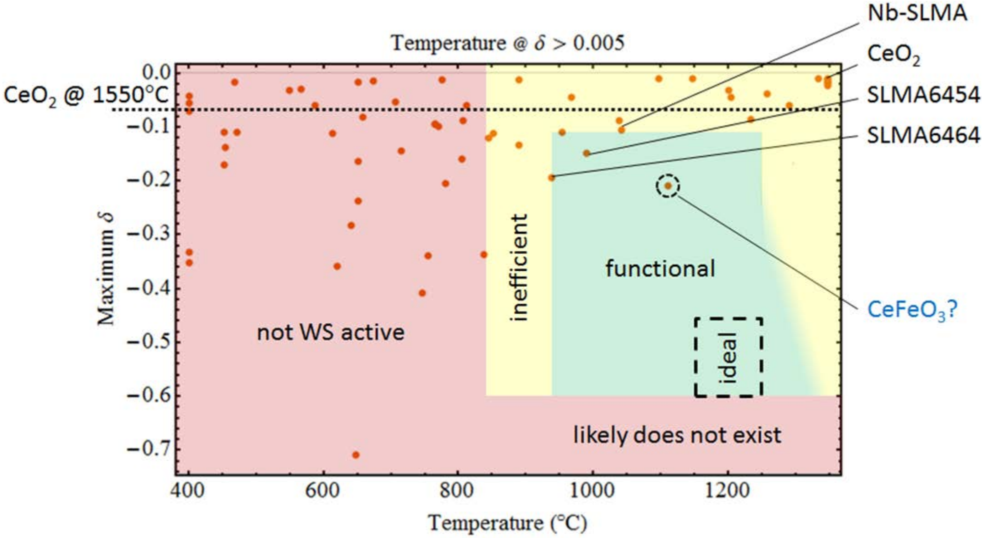
- Staged buildout and component testing through end FY16.
- Validation test of solar receivers at DLR's high-flux simulator.

Sandia National Laboratories

Technical Accomplishments and Progress

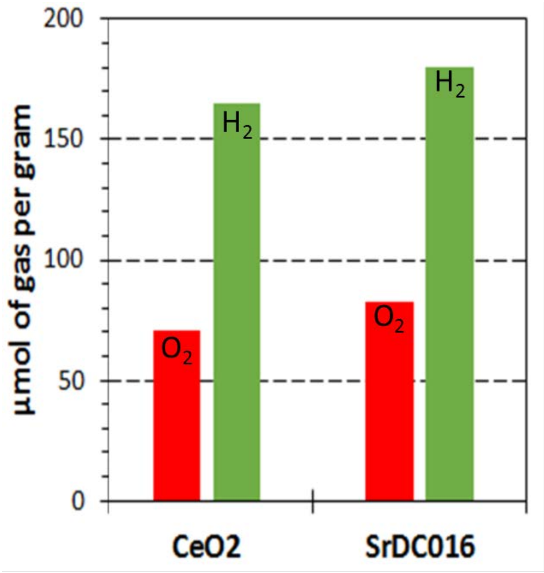
Combined DFT + Experiments to Accelerate Material Discovery

merit test based on max achievable δ vs. O_2 onset temperature



- **Screened ~50 new compounds.**
- **Discovered 5 new WS perovskites.**
- **Improved SLMA by Nb-doping.**
- **$CeFeO_3$ predicted by DFT.**
  - Mixed phase and cycle-unstable

10% increase in H_2 production with 1.6mol% Sr added to CeO_2

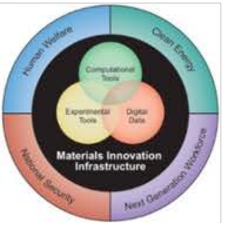


- **Engineered thermodynamics by adding small amounts of dopant.**
  - Raise configurational entropy through lattice softening
- **Sr-CeO_2 a successful case study.**

- **Refine approach to material discovery using DFT.**

Technical Accomplishments and Progress

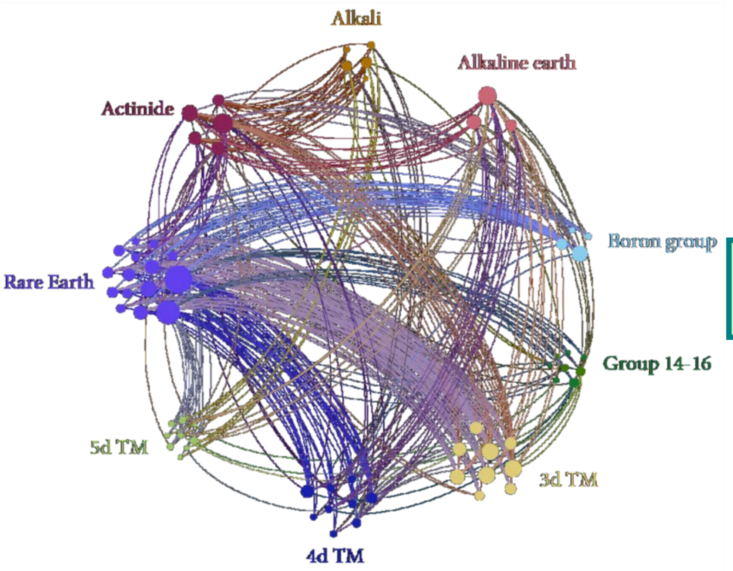
Advanced Materials Manufacturing (AMM) / Materials Genome initiative (MGI)



Innovative materials discovery and development for faster product development.
Key elements include:

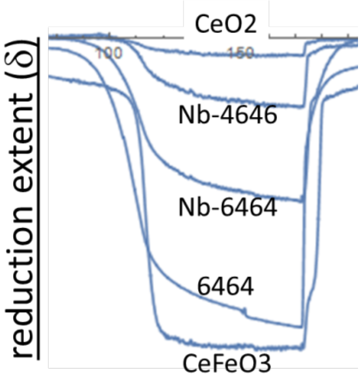
- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

ABO$_3$ network map

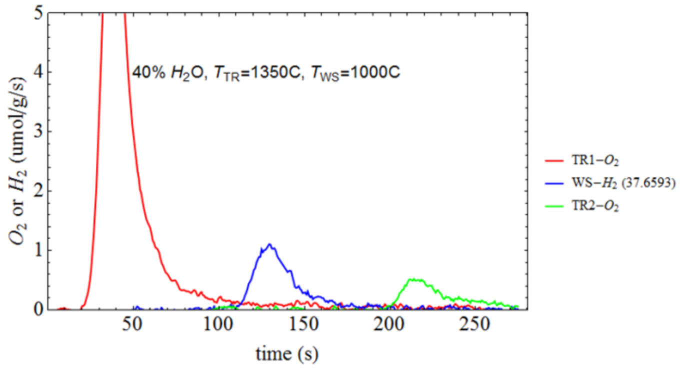


Paper by Wolverton group in review.

Formula	B-site
LaCoO3	Co
CeCoO3	Co
YCrO3	Cr
CeCrO3	Cr
LaCrO3	Cr
YFeO3	Fe
LaFeO3	Fe
CeFeO3	Fe
YMnO3	Mn
LaMnO3	Mn
CeMnO3	Mn
NaMoO3	Mo
SrSnO3	Sn
BaSnO3	Sn
CaVO3	V
SrVO3	V
YVO3	V
CeVO3	V
LaVO3	V



CeFeO$_3$:
Mixed phase
Ce^{+4} unstable A-site
Incomplete H_2O rxn
Cycle unstable

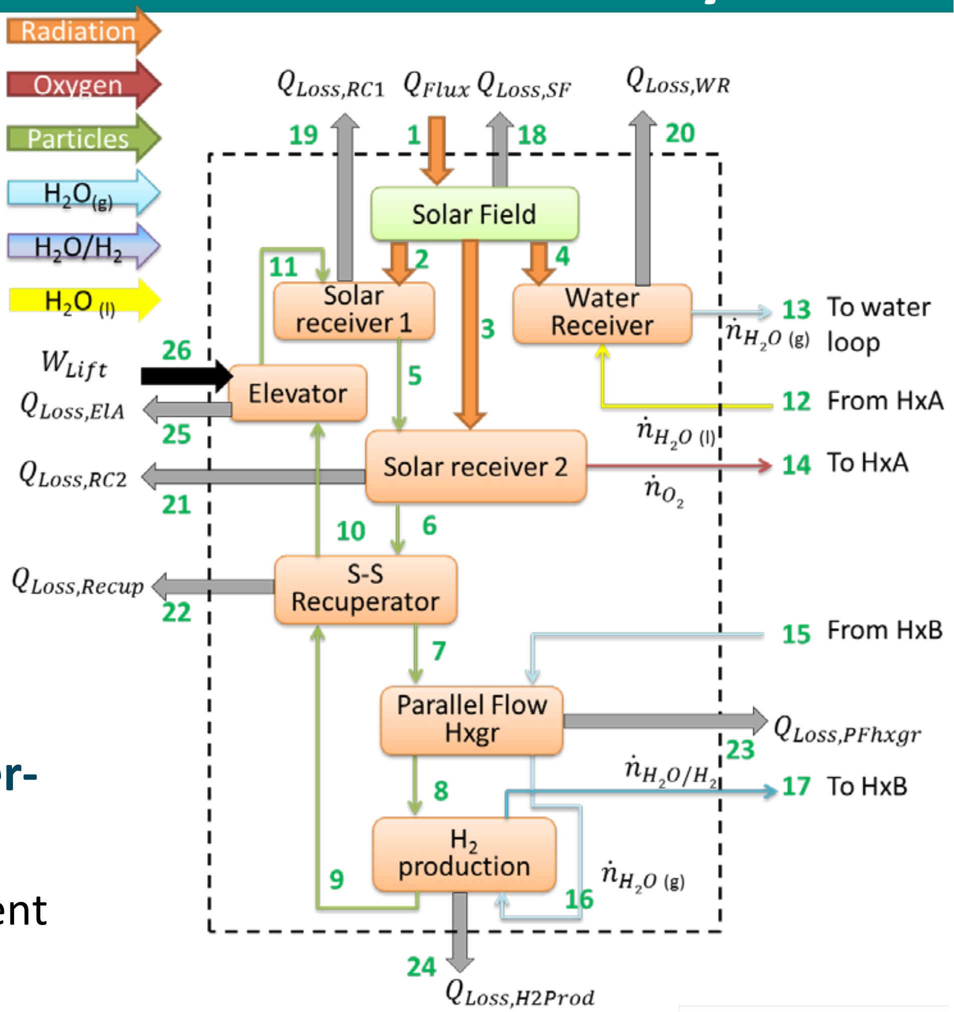


- **High throughput DFT of 11,000 calculated simple ABO$_3$ structures.**
  - 5400 stable oxides filtered to 19 possible WS-active compounds

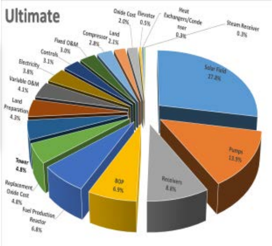
- **Evaluate the WS potential for all possible binary perovskites.**

Enabling Component-level Technoeconomic Analysis

- **Quasi-steady state model that dynamically follows DNI.**
- **Detailed receiver-reactor system with 8 major components.**
  - Account for mass and energy flows
  - Separate solar receivers for particle heating and reduction
  - Counter-flow H_2 production reactor
  - Heat exchange and recuperation
- **Exercising model with various water-loop configurations.**
  - System needs are material dependent



- **Goal to add fidelity and accuracy to H2A cost analysis.**
- **Conduct sensitivity and cost-performance tradeoff analysis.**



Response to Previous Year Reviewer’s Comments

FY15 Comments	FY16 Response
Materials discovery work may be an ever-expanding universe of investigations, rather than one converging on a viable solution for CPR2 testing during the scope of the project. Primary focus for this project should be on performing the reactor tests and demonstrating achievement of the project objective to produce 3 Liters of Hydrogen in 8 hours.	To mitigate this risk, we have confidence that the FOA milestone can be achieved with known materials. Nonetheless, the reviewer comments and the community continue to suggest needing both reactor and materials development. In this project we do our level best to move forward on both fronts.
Development of any efficient cost-effective direct solar processes for water splitting has the potential to provide a significant expansion of the role of solar energy. This solar thermochemical technology represents one possible pathway for direct solar hydrogen. But it is fraught with several extremely challenging technical issues, from the performance of the redox material, circulation of very high temperature solid particulates, selection of very high-temperature reactor materials, radiative heating of solid particles, etc.. Furthermore, the potential for high-efficiency performance is limited.	Disagree. The reason we are taking such a serious look at, and making investments in, this technology is because of the potential for high-efficiency performance. STCH potential for high-efficiency theoretically exceeds that of PV + electrolysis and PEC. Furthermore, great strides are being made by research groups around the world to advance the TRL of CSP for generating both electricity and industrial process heat.
Barriers have been identified and addressed and the technical approach to materials design and laboratory reactor testing is feasible, if challenging. The project partners have well defined roles in contributing to success of the project. However the scope of the project does not seem appropriately scaled to the project duration and available funding.	Agree. This two year effort is extremely ambitious. We have already accomplished a great deal of work, and are moving rapidly towards meeting our main demonstration milestone. Sandia looks on this project as a means to elevate and propel our core capability, and remain optimistic that we will have the opportunity to continue advancing this technology’s TRL.

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

Sandia's Laser-Heated Stagnation Flow Reactor now a virtual laboratory

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

7 Research Institutions in 4 time zones on 2 continents

Remaining Challenges and Barriers

Challenge

- **Discovering a redox material that will meet or exceed a STH efficiency of 5% in the CPR2, or will meet or exceed the 2020 target of 20%.**
- **Cannot verify the CPR2 design will meet or exceed 5% STH efficiency operating at ~3kW before construction.**
  - It is not possible to know with certainty that design choices will meet performance criteria until actually tested

Mitigation Strategy

- **Use CeO_2 in the CPR2 test.**
  - CeO_2 will satisfy the project milestone of 3L H_2 in 8 hours
- **Sub-component modeling and experiments will be used to verify design decisions.**
  - Project milestone of 3L H_2 in 8 hours will be met even if the STH efficiency is less than 5% in the CPR2
- **Detailed systems analysis and "Learn By Doing" will improve STH efficiency and show clear pathway to commercialization.**

Proposed Future Work

Remainder of FY16:

- **Produce ~150 kg of CeO_2 particulates (~300µm diam.) for CPR2 tests.**
  - Choice based on outcome of FY15 material decision point

- **Publish results on material discovery R&D in peer-reviewed journals.**

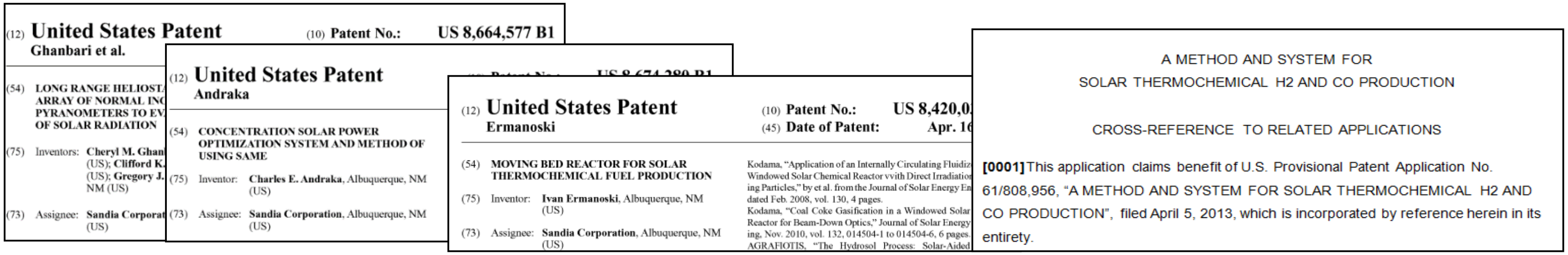
- **Fabricate components, assemble, and test CPR2 “on-sun”.**
  - Run at least 8 continuous hours at ~3kW producing more than 3L H_2
  - Satisfy project milestone by end of calendar year (FY17Q1)

- **Conduct full technoeconomic analysis of a 10^5 kg H_2/day plant.**
  - Extend/validate H2A result
  - Conduct detailed sensitivity and trade-off analysis

- **Publish results on technoeconomic analysis in peer-reviewed journals.**

Technology Transfer Activities

- **Collaborating with CoorsTek to produce large batches of redox active materials to support CPR2 test.**
  - Large supplier of ceramic and advanced materials to many industries
  - 50 production facilities in 14 countries on four continents
  - Using pilot proppant plant to make pelletized materials for CPR2
- **Sandia holds several patents on CSP, materials, and reactor technology.**



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

(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** (10) **Patent No.:** **US 8,420,0**
Ermanoski (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.**
  - Roadmap based on demonstration, advancing TRL, and economic analysis

Sandia National Laboratories

Summary

- **Completed CPR2 design and components are in fabrication.**
  - Validated design choices using modeling, simulation, and lab tests in order to reduce risk of reactor failure
  - Solar receivers will be tested in DLR's high-flux simulator
  - Reactor will demonstrate efficient H_2 production using a pressure cascade and countercurrent mass flow in WS chamber
- **Extended approach to material discovery and engineering of thermochemical properties.**
  - Demonstrated entropy engineering concept using Sr-CeO_2 showing a 10% increase in H_2 productivity with 1.6mol% addition of Sr
  - Applied DFT to guide synthesis and characterization of binary ABO_3 perovskites likely excluding simple oxides as viable candidates for efficient WS materials
- **Developed a component-level model of Sandia's STCH reactor concept to enable more advanced technoeconomic analysis.**
  - Add fidelity and accuracy to H2A cost analysis
  - Conduct sensitivity and cost-performance tradeoff analysis

FY16 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.

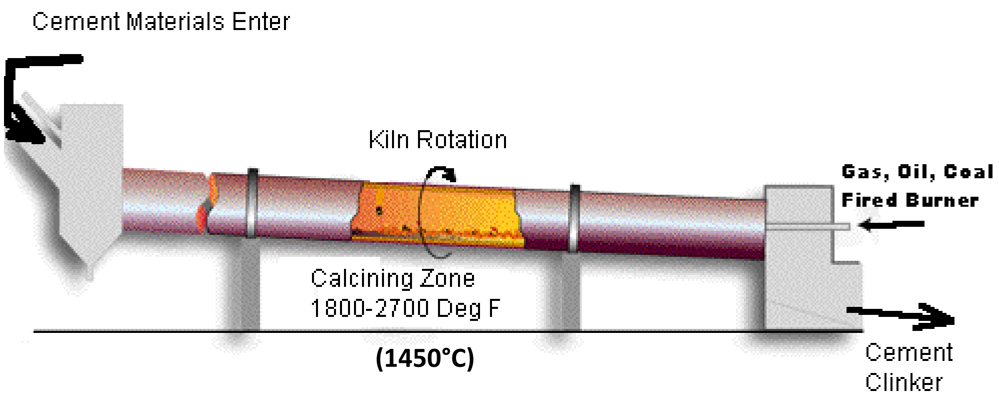
Thank You.

Questions?

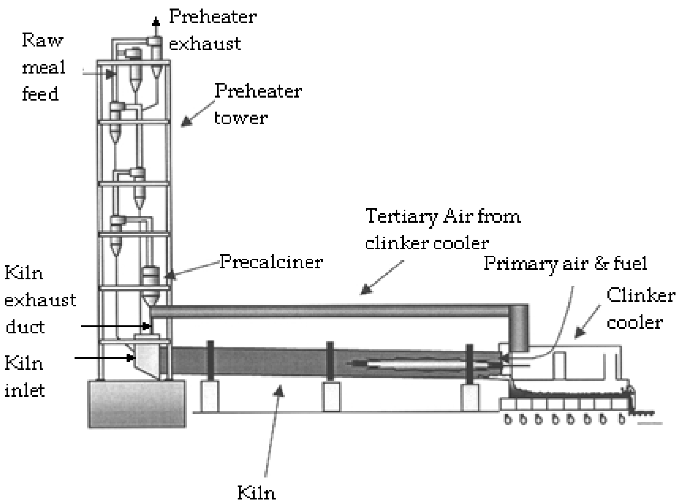
Sandia National Laboratories

Technical Back-Up Slides

STCH Technology Similar to Cement Manufacture

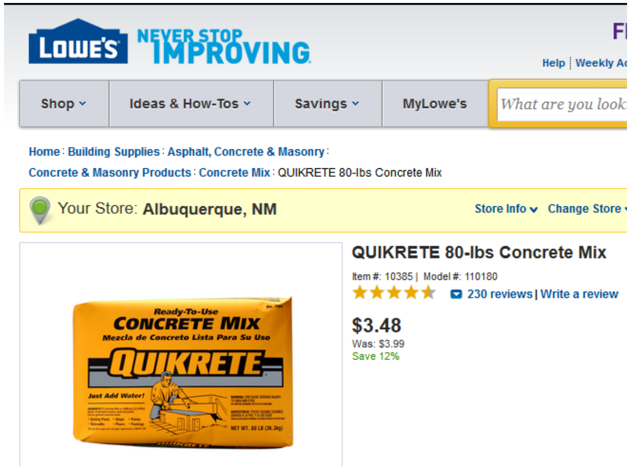


Kiln capacity: exceeding 10 000 tons of clinker per day



Chinyama, M. P. M., 2011, *Alternative Fuels in Cement Manufacturing*

- **Operating at 1450°C for years**
- **Lifts ~15 000 000 kg raw material per day (or about 10 000 kg/min)**
- **Conducts a thermochemical reaction: $CaCO_3 \rightarrow CaO$**
- **Fuel (natural gas) must be purchased and is part of the operating cost**



Home : Building Supplies : Asphalt, Concrete & Masonry : Concrete & Masonry Products : Concrete Mix : QUIKRETE 80-lbs Concrete Mix

Your Store: **Albuquerque, NM**

QUIKRETE 80-lbs Concrete Mix

Item #: 10385 | Model #: 110180

230 reviews | Write a review

$3.48

Was: $3.99

Save 12%

- **Bottom line: 15¢/kg cement – retail!**

STCH Technology Simpler than Gas Turbines

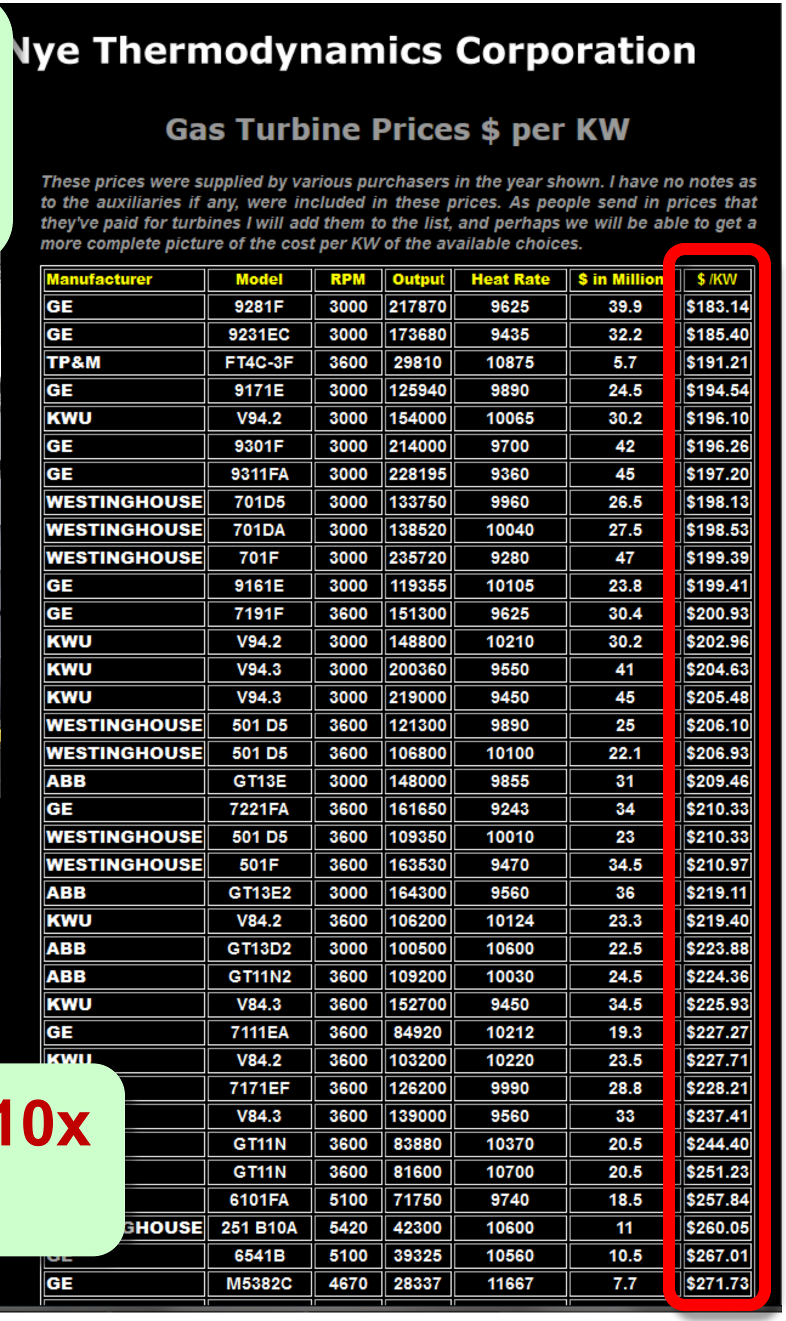
Heat engines are inexpensive, even gas turbines:

- **High temperature operation – up to 1650°C**
- **High speed – 10 000 to 500 000 RPM**
- **High pressure – exceeds 30 MPa**

Cost: 18-30 ¢/W

Compare to PV, DOE 2020 target of 100 ¢/W and 300 ¢/W current price

- **Bottom line: heat engines are 10x cheaper than PV**



Nye Thermodynamics Corporation

Gas Turbine Prices $ per KW

These prices were supplied by various purchasers in the year shown. I have no notes as to the auxiliaries if any, were included in these prices. As people send in prices that they've paid for turbines I will add them to the list, and perhaps we will be able to get a more complete picture of the cost per KW of the available choices.

Manufacturer	Model	RPM	Output	Heat Rate	$ in Million	$ /KW
GE	9281F	3000	217870	9625	39.9	$183.14
GE	9231EC	3000	173680	9435	32.2	$185.40
TP&M	FT4C-3F	3600	29810	10875	5.7	$191.21
GE	9171E	3000	125940	9890	24.5	$194.54
KWU	V94.2	3000	154000	10065	30.2	$196.10
GE	9301F	3000	214000	9700	42	$196.26
GE	9311FA	3000	228195	9360	45	$197.20
WESTINGHOUSE	701D5	3000	133750	9960	26.5	$198.13
WESTINGHOUSE	701DA	3000	138520	10040	27.5	$198.53
WESTINGHOUSE	701F	3000	235720	9280	47	$199.39
GE	9161E	3000	119355	10105	23.8	$199.41
GE	7191F	3600	151300	9625	30.4	$200.93
KWU	V94.2	3000	148800	10210	30.2	$202.96
KWU	V94.3	3000	200360	9550	41	$204.63
KWU	V94.3	3000	219000	9450	45	$205.48
WESTINGHOUSE	501 D5	3600	121300	9890	25	$206.10
WESTINGHOUSE	501 D5	3600	106800	10100	22.1	$206.93
ABB	GT13E	3000	148000	9855	31	$209.46
GE	7221FA	3600	161650	9243	34	$210.33
WESTINGHOUSE	501 D5	3600	109350	10010	23	$210.33
WESTINGHOUSE	501F	3600	163530	9470	34.5	$210.97
ABB	GT13E2	3000	164300	9560	36	$219.11
KWU	V84.2	3600	106200	10124	23.3	$219.40
ABB	GT13D2	3000	100500	10600	22.5	$223.88
ABB	GT11N2	3600	109200	10030	24.5	$224.36
KWU	V84.3	3600	152700	9450	34.5	$225.93
GE	7111EA	3600	84920	10212	19.3	$227.27
KWU	V84.2	3600	103200	10220	23.5	$227.71
	7171EF	3600	126200	9990	28.8	$228.21
	V84.3	3600	139000	9560	33	$237.41
	GT11N	3600	83880	10370	20.5	$244.40
	GT11N	3600	81600	10700	20.5	$251.23
	6101FA	5100	71750	9740	18.5	$257.84
GHOUSE	251 B10A	5420	42300	10600	11	$260.05
	6541B	5100	39325	10560	10.5	$267.01
GE	M5382C	4670	28337	11667	7.7	$271.73

Fuel Production Reactor Modeling

- **Material's model parameterized so new materials can be incorporated readily**
  - New fuel-production model
  - Departs from an assumption of equilibrium
  - Option to include none, all, or part of the exothermic heat from the re-oxidation reaction

$\dot{n}_g = ((\delta_{red} - \delta_{ox}) \cdot (\zeta + 1)) \cdot \dot{n}_p$

$\dot{n}_g$ = Gas stream molar flowrate

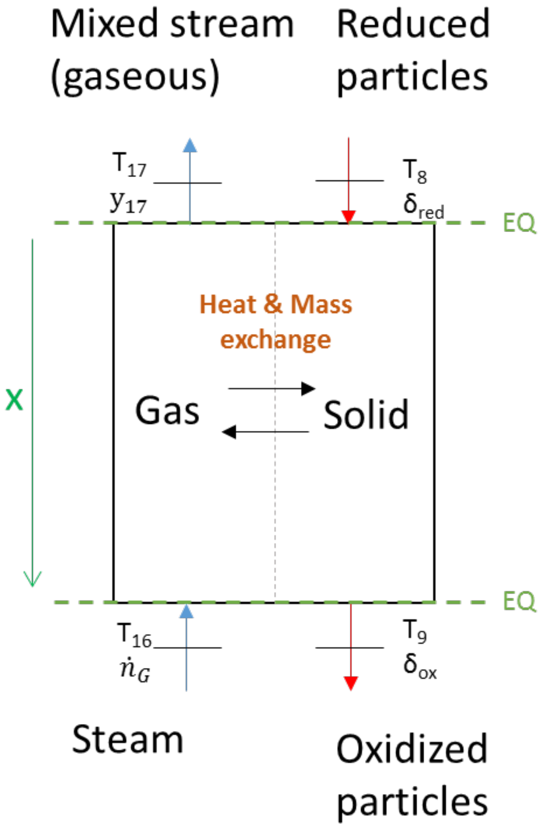
δ_{red} = Reduction extent from solar receiver

δ_{ox} = Re-oxidation extent

ζ = Zeta > minimum flow necessary

$\dot{n}_p$ = Particle molar flowrate

y_{17} = Percentage H2 in exiting stream



- **Quasi-steady state modelling while dynamically following DNI input.**