High Efficiency Solar Thermochemical Reactor for Hydrogen Production

Anthony McDaniel, Ivan Ermanoski

Sandia National Laboratories

DOE Annual Merit Review
11.06.2015

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.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Sandia National Laboratories

Overview

Timeline

- Project Start Date: 10/01/2014
- Project End Date: 10/01/2016
- Project Complete: 25%

Budget

- Total Project Budget.
  $2.600M
- Total Recipient Share.
  $0.243M
- Total Federal Share.
  $2.357M
- Total DOE Funds Spent:*
  $0.391M

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

- 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 Jianhua Tong
- Northwestern University, Evanston IL.
  - Prof. Christopher Wolverton
- Stanford University, Stanford CA.
  - Prof. William Chueh

Sandia National Laboratories

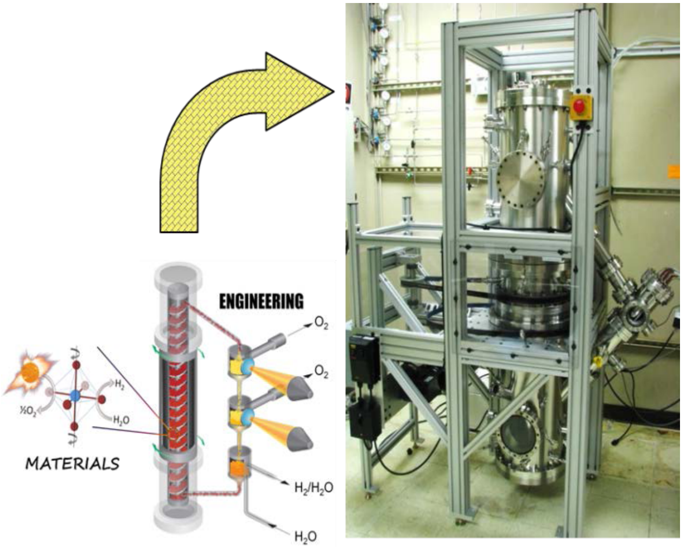
*As of 03/31/15

Relevance

•**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 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 2015 Objectives:**
  - Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. (**Barrier S & T**)
  - Design a particle receiver-reactor capable of continuous operation at 3kW thermal input. (**Barrier T & AC**)
  - Develop a detailed unit operations model of a large scale single tower, multiple receiver solar thermochemical reactor. (**Barrier X**)



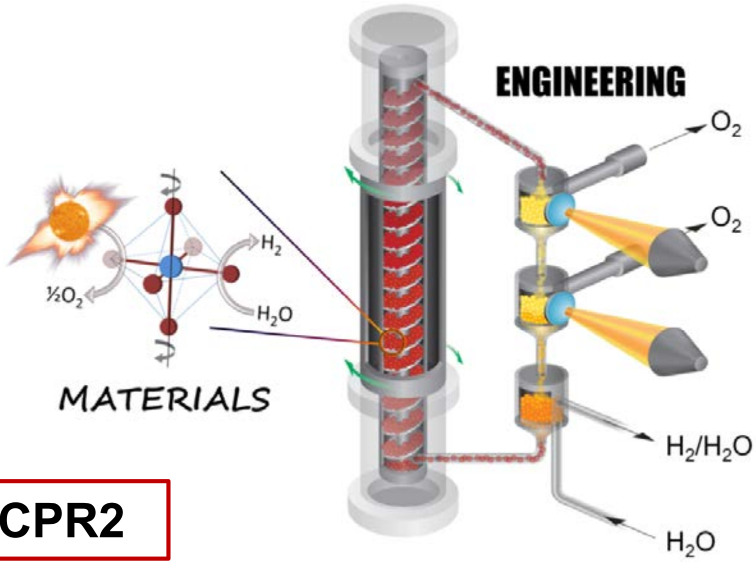
Reactor and Materials Innovation

- **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 reactor-material synergies
  - Reducing dependence on high-temperature solid-solid heat recovery

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \qquad \text{(1) Reduction}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \qquad \text{(2) Oxidation}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \qquad \text{(3) Thermolysis}$$



Cascading **P**ressure **R**eactor/**R**eceiver = **CPR2**

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

Sandia National Laboratories

Progress Metrics

10.2014-03.2015 Accomplishments

Q1	Q2	Q3	Q4

- Formulate and synthesize redox active oxides from doped $LaAlO_3$. (variants of La-Sr-Mn system) — **70%**
- Formulate and synthesize redox active oxides from earth abundant elements. (explore Fe, Mn, Ti, V redox systems) — **25%**
- Formulate and synthesize redox active oxides from $A_2B_2O_9$ crystal structure. (explore Mo redox system) — **10%**
- Characterize thermodynamic, kinetic, and other relevant properties of newly synthesized materials. — **25%**
- Build-out of particle elevator, demonstrate continuous particle flow >10 g/s, pressure separation >25kPa, vacuum pressure of <1kPa, and particle T>300°C. — **80%**
- Design and construct ~7kW solar simulator at Sandia capable of supplying heat to CPR2 solar receivers operating at T~1500°C, and at p<1kPa. — **20%**
- Develop designs for CPR2 solar-particle interface and reduction chambers. — **60%**
- Finalize CPR2 design. — **30%**
- Develop mass and energy flow models of large scale H_2 production plant. High-level, one-dimensional, steady state models of discrete unit operations. — **50%**

MATERIALS **REACTOR** **ANALYSIS**

Sandia National Laboratories

Milestones

10.2014-03.2015 Accomplishments

ACTIVITY	MILESTONE	COMPLETE
Discover new redox material	New perovskite material will have a redox capacity >> 250 micromole H2/g material, that reduces effectively at T < 1623K (threshold established by SLMA), and has kinetics and thermodynamics tuned for optimal STH efficiency (> 10%) in a particle bed reactor.	**0%**
Produce CPR2 engineering drawings and show it can meet >5%STH efficiency at<5kW.	**S**pecific (engineering drawings are tangible items that are sufficiently detailed so that a skilled machinist can cut, weld, bend, etc. metal, glass, and other materials to produce a 3-D rendering from the CPR2 design) **M**easureable (the design will create a reactor capable of operating at an STH efficiency >5% on the 2-5kW scale. Ultimately this will be measured and validated when the CPR2 is fabricated and tested. However, in design space the CPR2 performance will be extrapolated from simple experiments that test for criteria compliance. For example, 5% STH at 3kW = 150 J/s chemical. This translates into 0.83 L/min H_2 (based on LHV). The CPR2 will need to process $0.0006*MW_{oxide}/\Delta\delta$ of oxide [g/s]. MW_{oxide} is the molecular weight of the oxide in g/mol. Simple experiments used to test particle motion, heat transfer, and steam oxidation within and through designed components will measure this (among other things). **A**chievable (it is well within the skillset of our team provided that there are no issues with the DLR contracting process.) **R**elevant (drawings are absolutely critical to component fabrication and reactor assembly.) **T**imed (it is well within our project plan to complete this by end of year 1 provided that there are no issues with the DLR contracting process.)	**50%**

Engineering Material Thermochemistry

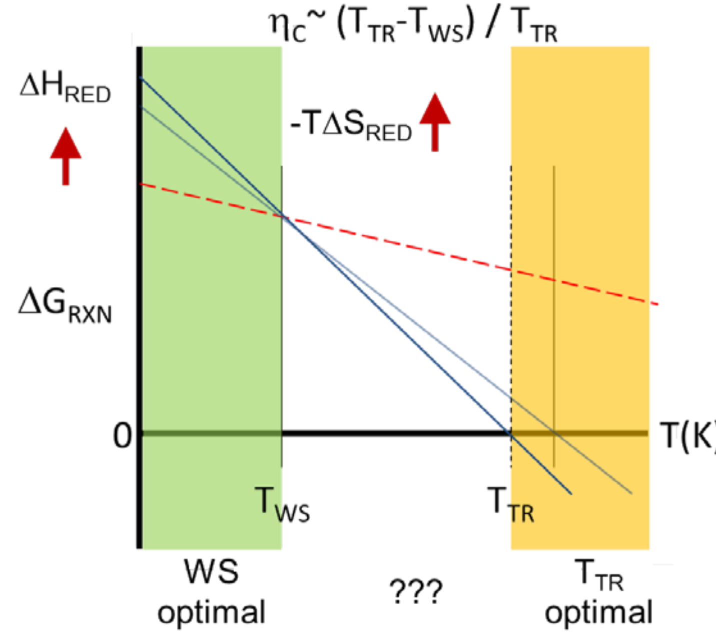
Why is it important?

- **Determines operating conditions.**
  - Heat flux, T_{TR}, T_{WS}
  - Mass fluxes: MO_x, steam, H_2
- **Determines cost of H_2.**
  - Plant design and operation
  - η_C is one component of STH efficiency

ΔH_{RXN} = y-intercept, ΔS_{RXN} = slope

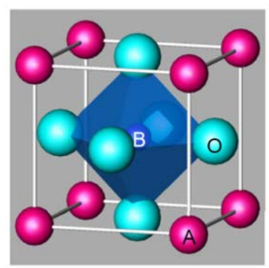
$\delta H_2O \rightarrow \delta H_2 + \delta/2 O_2$

$MO_x \rightarrow MO_{x-\delta} + \delta/2 O_2$



How is it done?

- **Identify candidate oxides.**
- **Manipulate crystal structure.**
  - A & B site doping
  - A & B site substitution
  - Introduce new phases

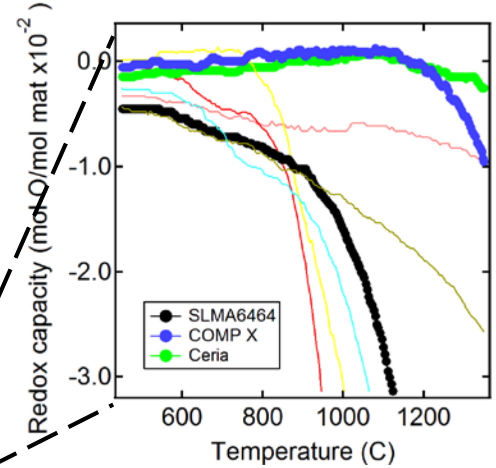


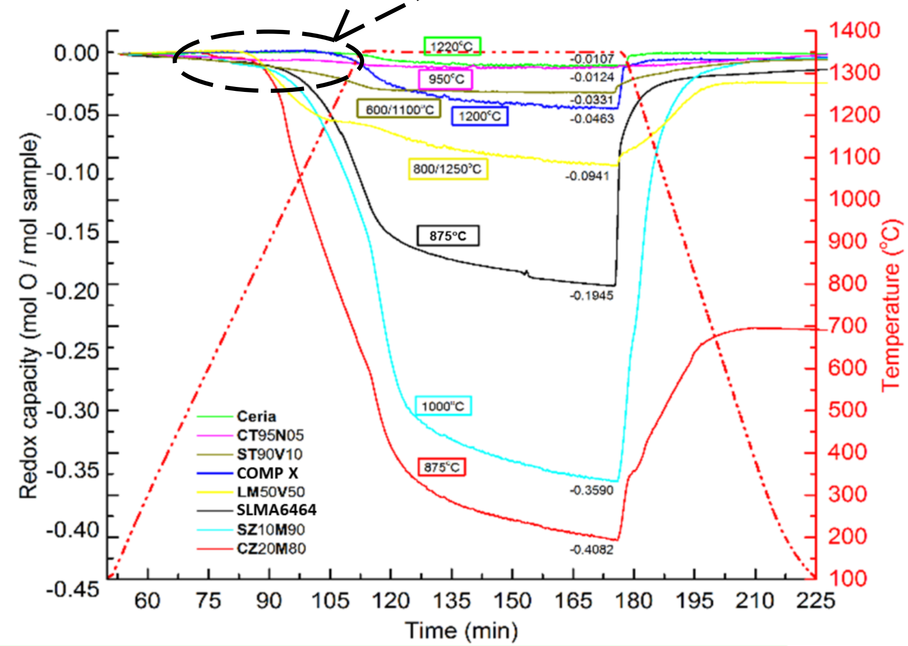
- **Reduce T_{TR} and optimize STH efficiency.**

Synthesis and Screening of Novel Compounds

- **Synthesized more than 50 new compounds.**
- **Explored redox activity of 1st row transition metals (TMs).**
  - Ti, V, Mn, Fe
- **Perovskite and similar crystal structures.**
  - ABO_3, ABO_4, $A_2B_2O_9$
- **Further developed an O_2-TPD screening protocol.**
  - Faster than TGA
  - Correlate onset of O_2 evolution to reduction enthalpy (ΔH_{RED}) and water-splitting activity

Material	T (C)	Capacity
SLMA6464	875	-0.2
COMP X	1150	-0.05
Ceria	1220	-0.01



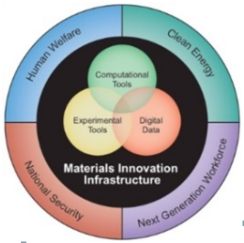


- **Discovered a doping strategy to improve SLMA performance.**

Sandia National Laboratories

Quantum Theory to Aid Understanding of Redox Behavior

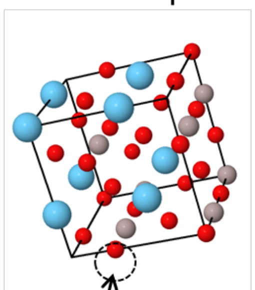
Advanced Materials Manufacturing (AMM) / Materials Genome initiative (MGI)



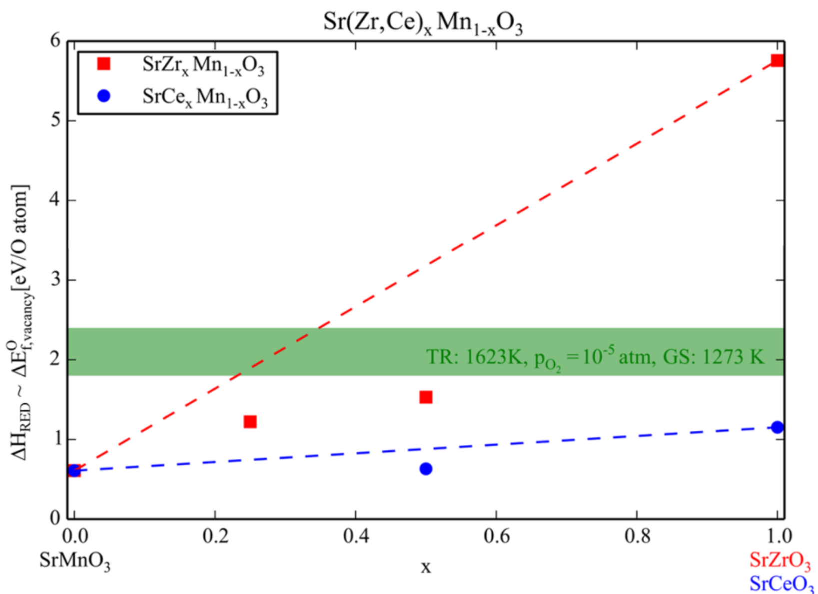
Innovative materials discovery and development for faster product development.
Key elements include:

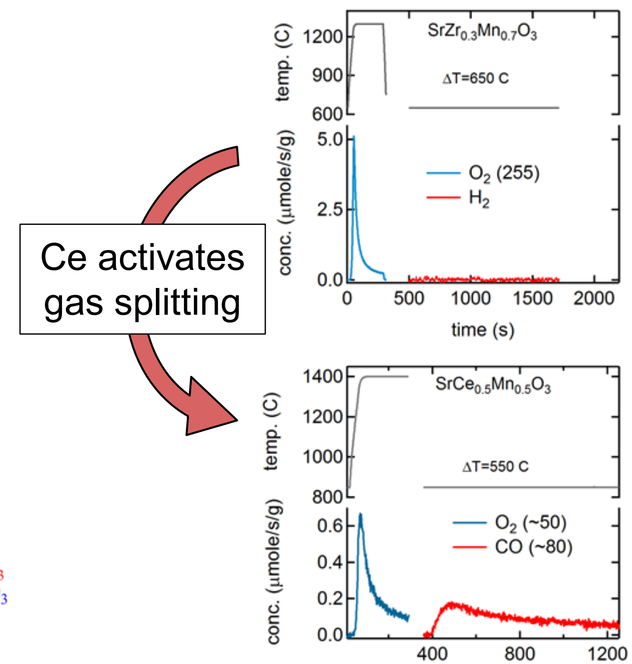
- **Integrating experiment, computation, and theory**
- **Making digital data accessible**
- **Creating a world-class materials workforce**
- **Leading a culture shift in materials research**

40-atom supercell



Calculate energy required to remove one O atom





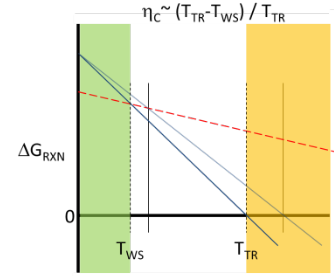
- **Validate Density Functional Theory (DFT+U) calculation against experiment.**
- **Use DFT simulations to find water-splitting compounds.**
  - Assess thermodynamic *descriptors* to RAPIDLY screen libraries of known structures

Engineering Entropy Instead of Enthalpy

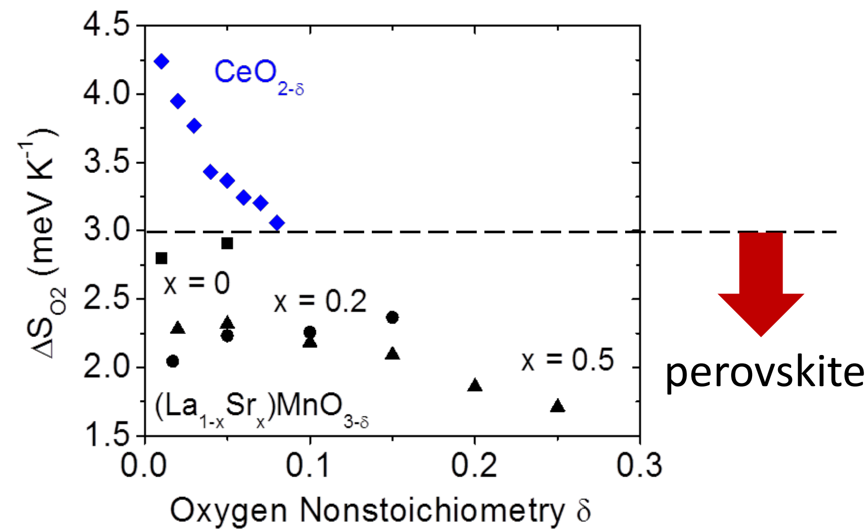
$$O_O^{\times} \xrightarrow{\Delta H_{red},\Delta S_{red}} V_O^{\bullet\bullet} + 2e' + \tfrac{1}{2}O_2$$

Gas phase entropy (fixed)

Solid state entropy (material specific)



- **$\Delta G = \Delta H - T\Delta S$**
  - $T\Delta S$ term is large at **high T**
  - Decrease T_{TR} more than T_{WS}
- **Raise configurational entropy of TM d-electrons by site doping.**
  - A site (lattice distortion)
  - B site (ligand field)
- **Raise vibrational entropy through lattice softening.**
  - Increase lattice volume on vacancy formation



Increase reduction entropy in perovskite:
- **Decrease T_{TR}**
- **Increase WS efficiency**

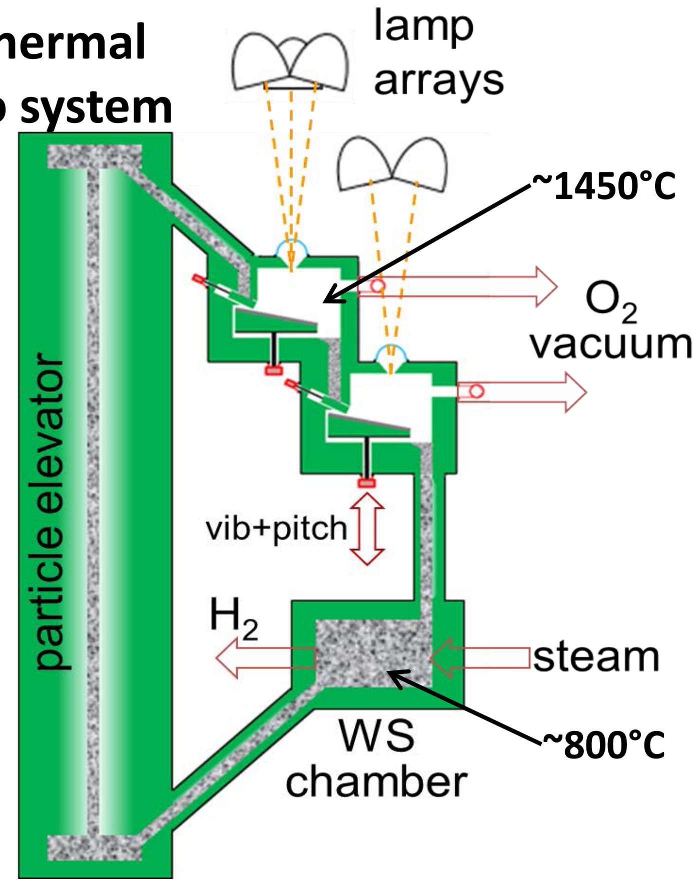
Sandia National Laboratories

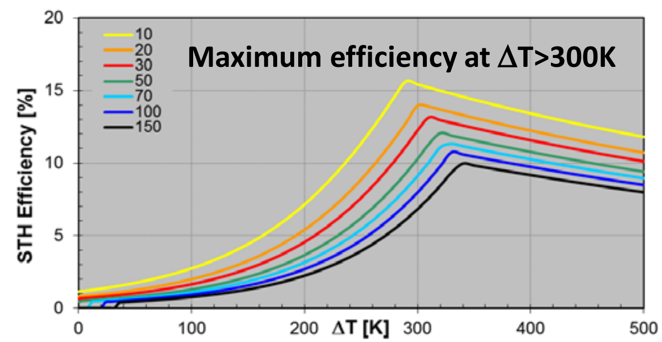
Cascading Pressure Reactor/Receiver (CPR2)

- **FOA requirement:**
  - 8 hours continuous operation
  - greater than 3 liters of H_2
- **High-efficiency attributes of CPR2.**
  - Pressure and temperature separation
  - Continuous operation
  - Pressure cascade to drive reduction extent
- **Finalized conceptual system design.**
  - Receiver configuration
  - Heat flux and heat transport
  - Oxide flow rate and control
  - Pumping requirements

- **Evaluated multiple receiver options.**
- **Established key design criteria.**

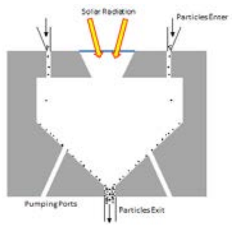
3kW thermal input to system

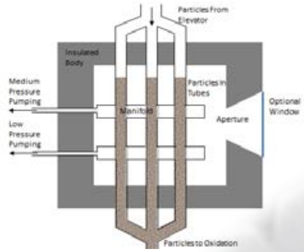


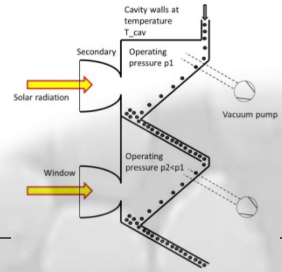


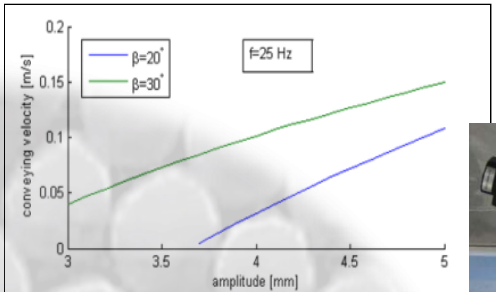
Sandia National Laboratories

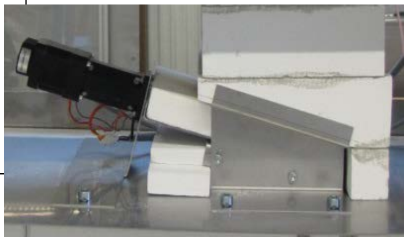
Designing the Solar Receiver

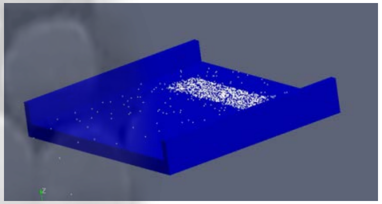






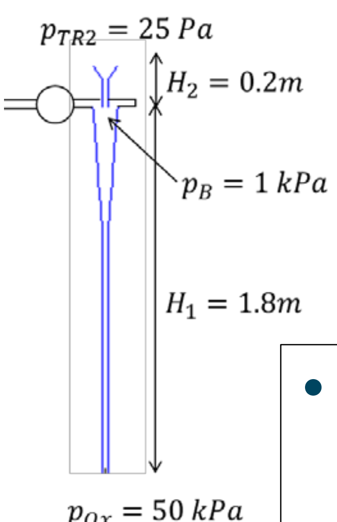


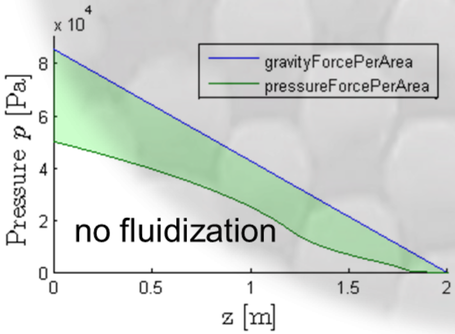




- **Solar interface.**
  - Direct or indirect particle irradiation
  - Beam-up or beam-down optics

$$\frac{\mathrm{d}p}{\mathrm{d}z} = -\frac{\dot{m}_g}{A(z)}\frac{RT}{pMD_p}\frac{1-\phi}{\phi^3}\left[\frac{150(1-\phi)\mu}{f_c\,(Kn)D_p} + 1.75\frac{\dot{m}_g}{A(z)}\right]$$





- **Particle flow control.**
  - Valves, vibrating plates, actuated drives

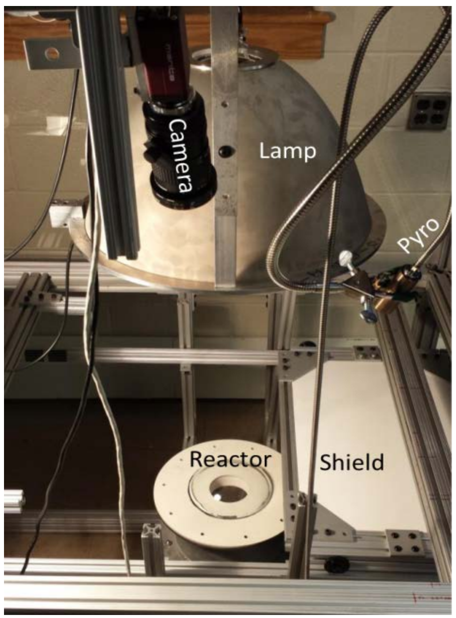
- **Pressure separation.**
  - Particle diameter and mass
  - Bed permeation and fluidization

- **Key design criteria established by detailed modeling when necessary.**

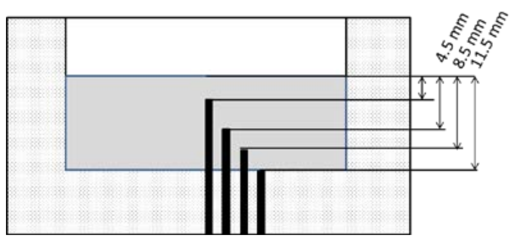
Sandia National Laboratories

Understanding Radiative Particle Heating

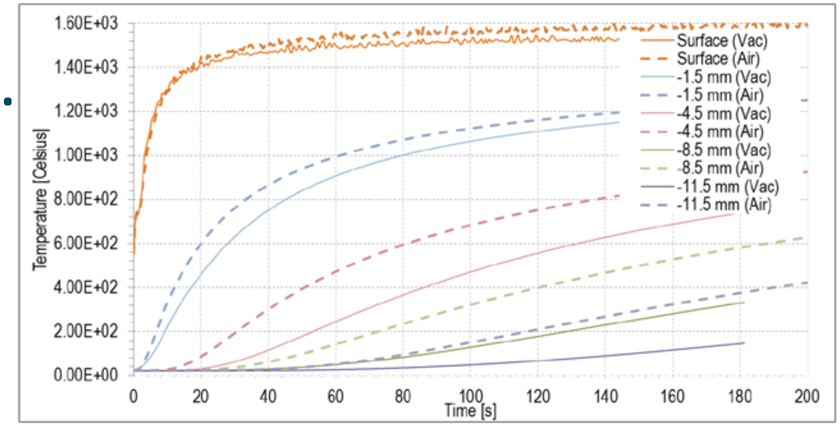
- **Vacuum lowers heat transfer efficiency.**
- **Static particle bed.**
  - Worst case scenario



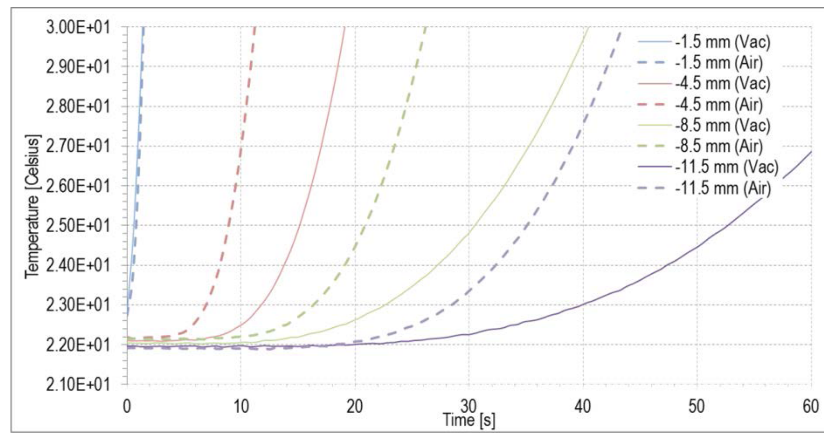
Experimental setup



Placement of TCs



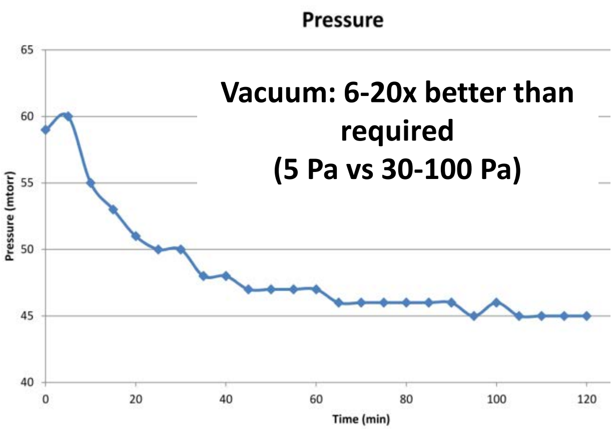
Heating rate

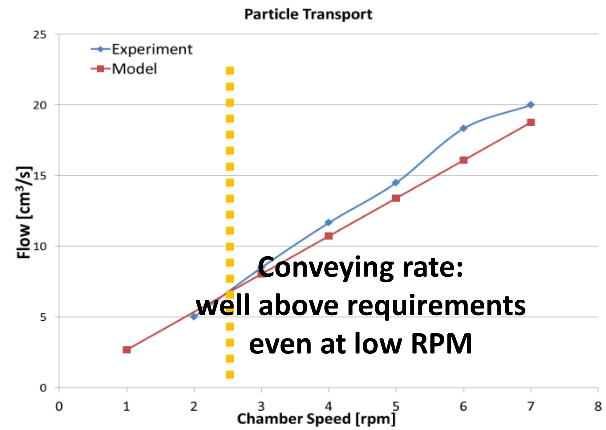


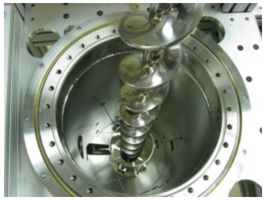
Heat propagation

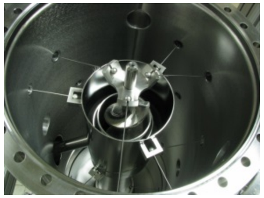
- **Qualified: Particle heating to 1500°C using simulated sunshine.**

CPR2: From Concept to Device

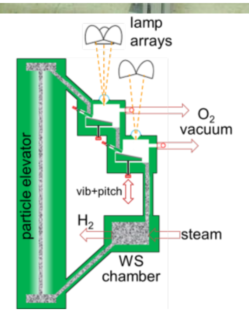








assembled vacuum elevator

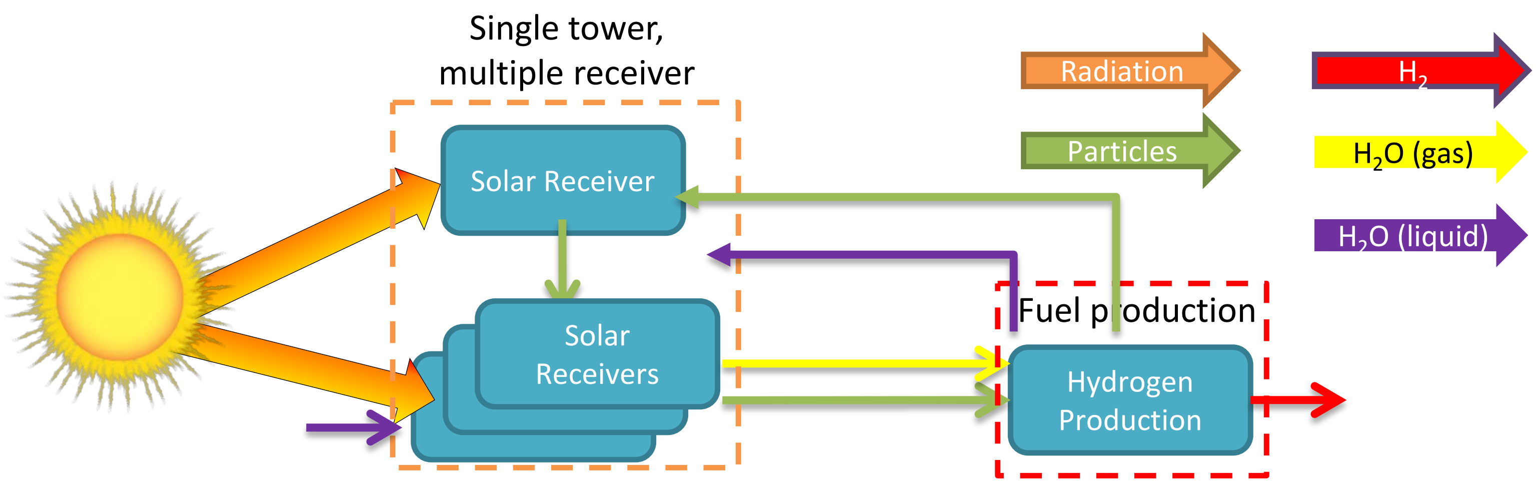


- **Particle transport via Olds™ lift design.**
  - Fixed auger, rotating wall
  - Mass conveying rate well above design requirements
- **Particle column establishes pressure separation.**
  - Rotating chamber seals maintain high vacuum
- **Particle lift will operate at T~800°C.**
  - Heating tests underway

- **Qualified: Particle conveyance and vacuum.**

Sandia National Laboratories

Improving Economic Analysis



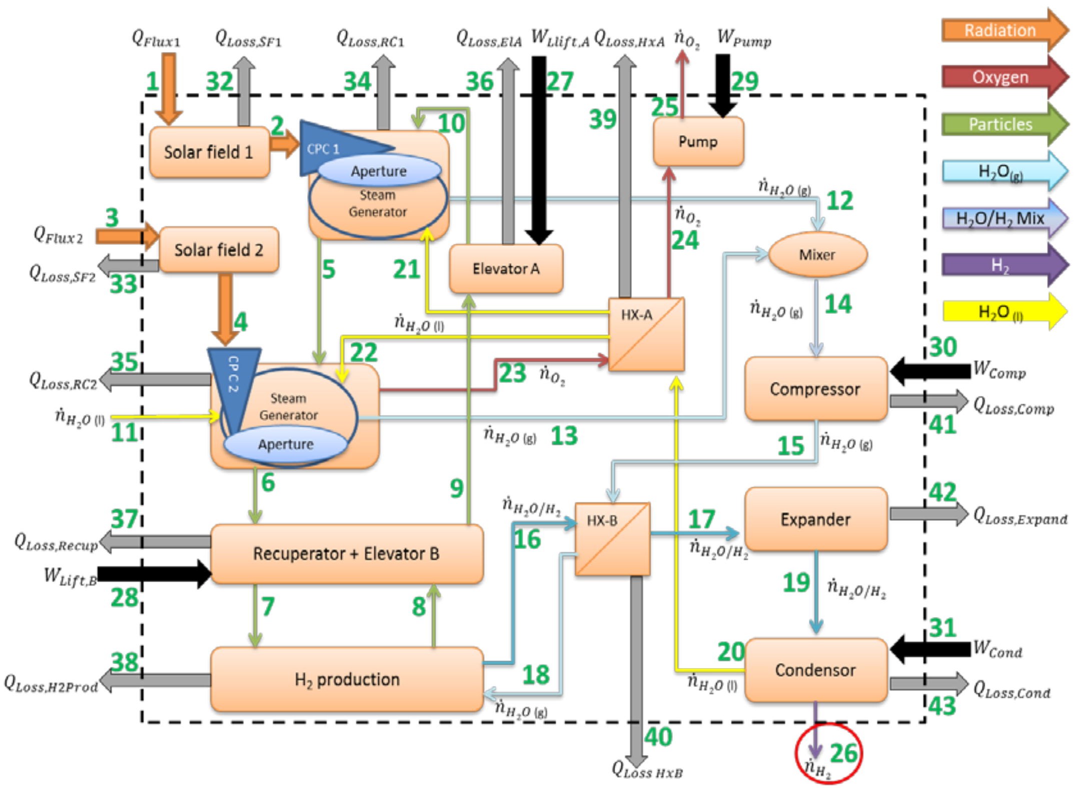
- **Add fidelity and accuracy to H2Av3 cost analysis.**
  - Verify the potential for solar thermochemical hydrogen production to be competitive in the long term
  - Conduct trade-off analysis on plant design and operation
- **Target H_2 production is 100,000 kg/day.**
  - Integrate H_2 production with CSP in a single tower, multiple receiver design

- **Leveraging CSP concepts development for integration with H_2 production.**

Establish Data Requirements and Inputs to Model

- **Single tower, multiple receiver model.**
  - 14 model elements
  - 43 mass and energy states
- **Calculate mass and energy flows at each solar insolation.**
  - Validation/upscaling data measured on 3kW reactor
- **Single tower is one of many in a large-scale plant design.**
  - ~230-four MW_{th} towers
  - located on 750 acres

Matlab™ implementation underway



- **This level of detail is currently lacking in H2Av3 analysis.**

Sandia National Laboratories

Collaborations

Material Discovery and Characterization Team

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

Reactor Design, Testing, and Demonstration Team

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

Systems Analysis Team

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

Remaining Challenges 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

Mitigation Strategy

- **Use SLMA or CeO_2 in the CPR2 test.**
  - Either of these materials 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
- **"Learn by doing" will improve STH efficiency and show clear pathway to commercialization.**

Sandia National Laboratories

Proposed Future Work

Remainder of FY2015

- **Continue material discovery and optimization R&D.**
  - Make decision on material for CPR2 test
- **Finalize CPR2 design and produce engineering drawings for fabrication.**
  - Develop detailed models of sub-component behavior as necessary to validate concepts
  - Conduct experiments of sub-component behavior as necessary to validate concepts
  - Satisfy FY15 project milestone
- **Design solar field and BOP for 10^5 kg H_2/day plant.**

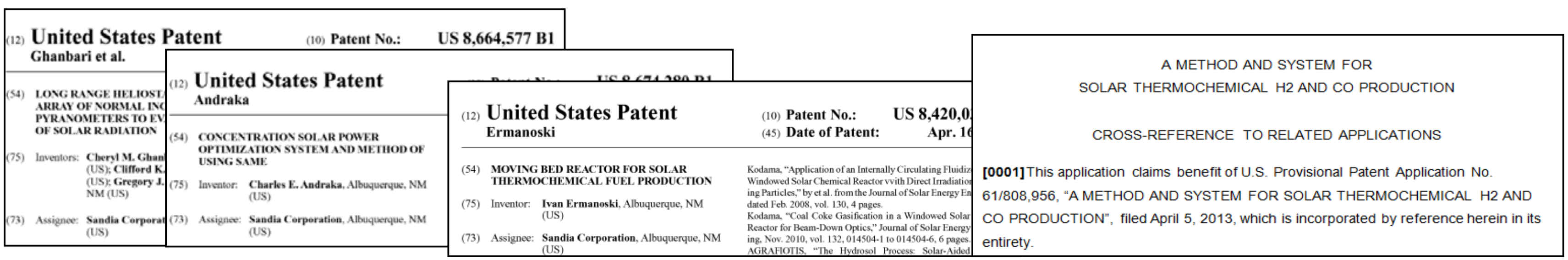
FY2016

- **Continue material discovery and optimization R&D.**
  - Develop thermodynamic and kinetic models of material performance
- **Produce ~100 kg of redox material for CPR2 tests.**
  - Choice based on outcome of FY15 material decision point.
- **Fabricate components, assemble, and test CPR2 "on-sun".**
  - Run at least 8 continuous hours at ~3kW producing more than 3L H_2
  - Satisfy FY16 project milestone
- **Full technoeconomic analysis of a 10^5 kg H_2/day plant.**
  - Based on a detailed model of up-scaled CPR2 performance, solar field, and BOP
  - Extend/Validate H2Av3 result, conduct detailed sensitivity and trade-off analysis

Sandia National Laboratories

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.**



- **Business interest exists from Olds Elevator LLC.**
- **Operating the CPR2 is paramount to technology transfer plan.**
  - Roadmap based on demonstration, advancing TRL, and economic analysis

Sandia National Laboratories

Summary

- **Extended approach to material discovery and engineering of thermochemical properties.**
  - Exploring several TM redox pairs (Fe, Mn, Mo, Ti, V)
  - Focused on entropy engineering to optimize material performance
  - Validating DFT theory against experiments to enable computational screening
- **Designing a 3kW cascading pressure reactor/receiver (CPR2).**
  - Established key criteria and down-selected receiver design
  - Windowed cavities, particle transport by gravity and vibration
  - Pressure separation achieves high STH efficiency
- **Assembled and tested Olds™ particle elevator.**
  - Qualified conveyance rates and vacuum separation
- **Established data requirements for single tower, multiple receiver reactor model for 10^5 kg H_2/day plant.**
  - Building unit-ops models for detailed technoeconomic analysis beyond H2Av3
  - Better model for establishing STCH criteria necessary for meeting DOE goals

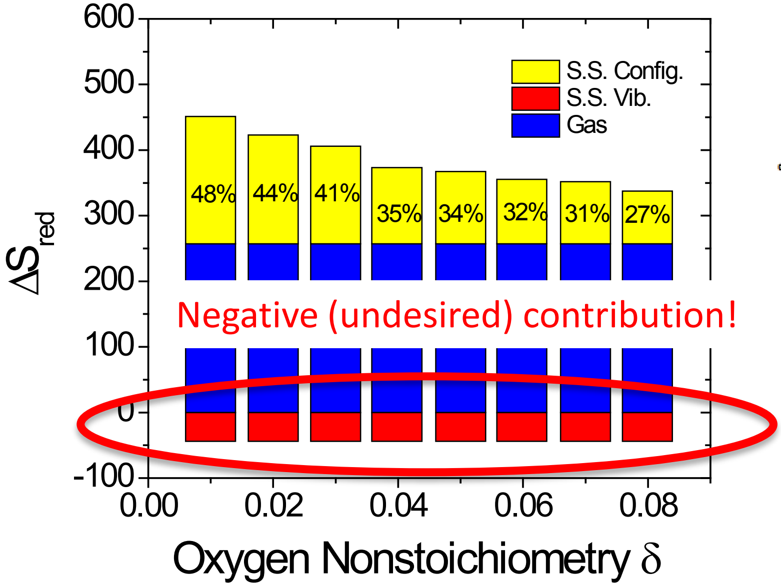
FY15 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.

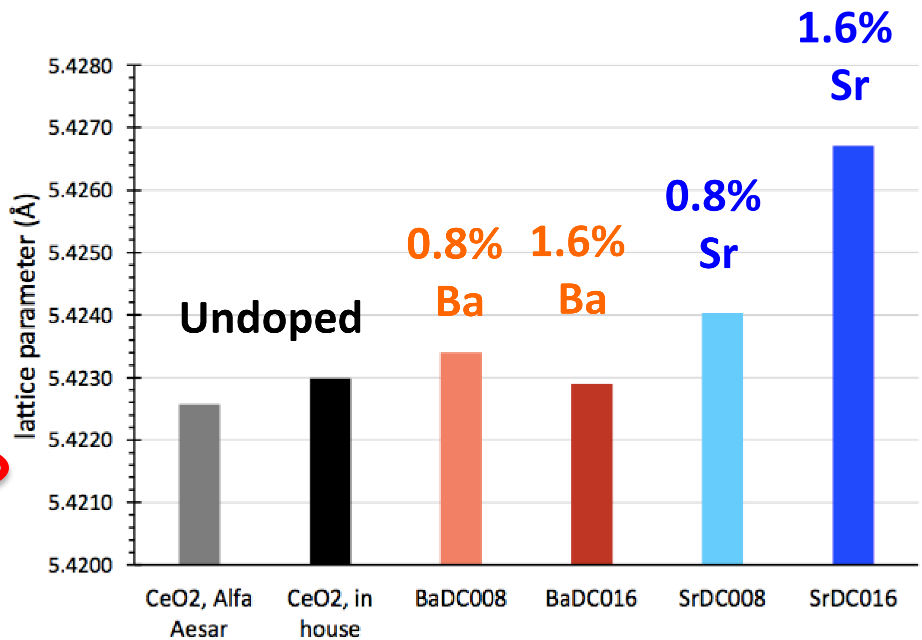
Thank You.

Questions?

Technical Back-Up Slides

CeO_2 Entropy Engineering Example





- **Vibrational reduction entropy of CeO_2 is <u>negative</u> which elevates the reduction temperature.**
- **We expect substituting CeO_2 with < 2% mol dopant of a large ionic radius will change the sign of the vibrational reduction entropy.**
  – Decrease the reduction temperature of ceria through low-level cation substitution

Sandia National Laboratories

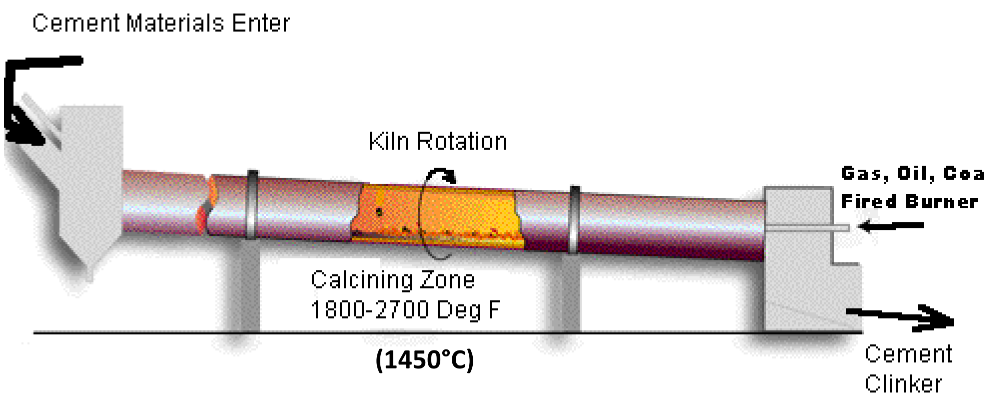
Systems Thermodynamic Modeling: Tower + Receivers

- MS-5.1 – Produce a list of data requirements and input needs for high-level unit operations models. Information pulled form all tasks. Model mass and energy flows at each solar isolation.

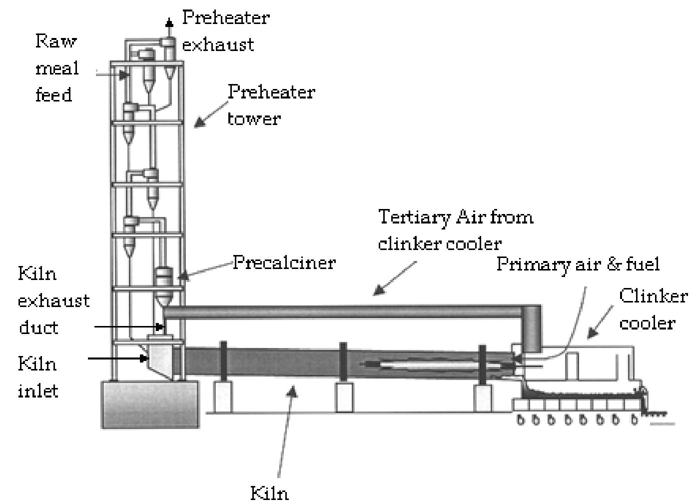
Variable	Value	Variable	Value
Solar Field	46325 m^2	Metal-oxide molar mass	216.1 g/mol
Solar field efficiency	60%	Metal-oxide specific heat	124.7 J / mol×K
Concentration Factor	3000	δ_{RC1} reduction extent	0.01
RC1 aperture area	4.5 m^2	$H_{rxn}(\delta_{RC1})$ heat of reduction reaction	820 kJ/ mol-O_2
RC1 re-radiation temp	1635 K	δ_{Ox} re-oxidation extent	0.01
RC1 emissivity	0.9	$H_{rxn}(\delta_{Ox})$	820 kJ/ mol-O_2
RC1 additional heat loss % of net radiation	5%	δ_{RC2} final reduction extent	0.25
RC1 particle outlet temp	1635 K	$H_{rxn}(\delta_{RC2})$	820 kJ/ mol-O_2
RC2 aperture area (total) Equivalent of 4 receivers D=1.1 m	Pi D^2 or ~3.8 m^2	T_0 (ambient temperature)	298 K
RC2 re-radiation temp	1635 K	P_0 (ambient pressure)	101,325 Pa
RC2 emissivity	0.9	P_{O2} (partial pressure of oxygen)	10 Pa
RC2 additional heat loss % of net radiation	5%	P_{RC2} (pressure of n^{th} receiver)	10 Pa
RC2 particle inlet temp	1635 K	T_{ox} (temperature of reoxidation)	1073 K
RC2 particle outlet temp	1635 K	Water (11) inlet temp	298 K
HxA heat transfer coeff.	12 W / m^2×K	Recuperator efficiency	50%
HxA contact area	5000 m^2	Elevator A height	11 m
HxB heat transfer coeff.	12 W / m^2×K	Elevator B height	8 m
HxB contact area	5000 m^2		

Sandia National Laboratories

STCH Technology Similar to Cement Manufacture

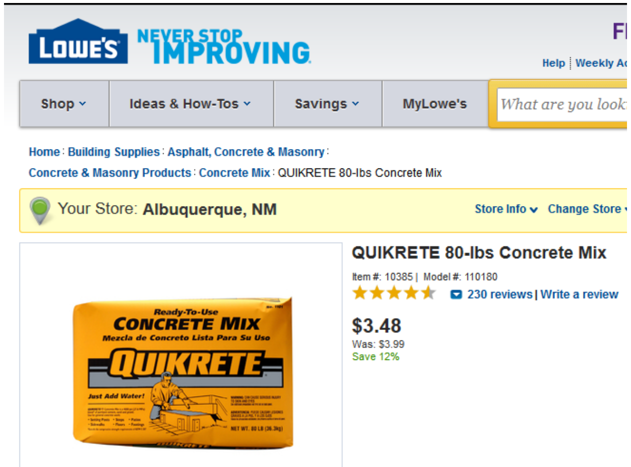


Kiln capacity: exceeding 10 000 tons of clinker per day



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**



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

Sandia National Laboratories

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
[illegible]	7171EF	3600	126200	9990	28.8	$228.21
[illegible]	V84.3	3600	139000	9560	33	$237.41
[illegible]	GT11N	3600	83880	10370	20.5	$244.40
[illegible]	GT11N	3600	81600	10700	20.5	$251.23
[illegible]	6101FA	5100	71750	9740	18.5	$257.84
GHOUSE	251 B10A	5420	42300	10600	11	$260.05
[illegible]	6541B	5100	39325	10560	10.5	$267.01
GE	M5382C	4670	28337	11667	7.7	$271.73

National Laboratories