Sunshine to Petrol

Thermochemical Reactor R&D

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Sandia National Laboratories

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Solar Thermochemical Fuel Systems

- Offer the potential to be considerably more efficient than current alternatives
- The majority of ongoing solar thermochemical research is based on two-step metal oxides
- A perfect material does not guarantee a successful system
- Thermochemical reactor development is challenging
- There are no reactors currently in existence that can beat the efficiency of solar (CSP or PV) electrolysis (many can't even do it on paper)

The Competition

- Molten salt power tower with alkaline electrolysis (~80% electric to H_2)
  - 14% annual average solar to hydrogen
  - 30% heat to hydrogen
- Dish Stirling with alkaline electrolysis
  - 19% annual average solar to hydrogen
  - 26% heat to hydrogen
- PV with alkaline electrolysis
  - 12% annual average solar to hydrogen

System Level Analysis

T_{TR}= 1500°C,T_{OX} = 1000°C
P_{TR} = 100 Pa

Sunlight

Resource eff.=(Resource>300 DNI)/Resource= **95%** for Daggett

Operational ~ 94%
Equip. Availability = 97%, B&S = 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 Available Heat = 58%

Reactor/Thermochemical ~ 37%
Pumping ~ 96% (100 Pa)

H_2

Annual Average Solar to Hydrogen
Design Point: 21%
Range: 20%-24%

System Level Conclusions

- Lots of opportunities to lose energy
  - Some improvement in collection is possible, but not much
- The reactor is the least efficient single component
  - Why? Can it be improved?
    - Better reactor: See “key attributes”
    - Better materials

Key Reactor Attributes

- Continuous operation on-sun
- Sensible energy recovery (recuperation)
- Minimal work input and pressure separation
- Direct solar absorption
- Chemical and mechanical durability
- Inherent reaction product separation

Reactor Development Summary

- We've developed two reactor concepts that embody most of the key design attributes, and are "reactant flexible".
- CR5
  - 10 kW_{th} prototype under test
- Particle reactor
  - In the design stage

Counter Rotating Ring Receiver Reactor Recuperator (CR5)

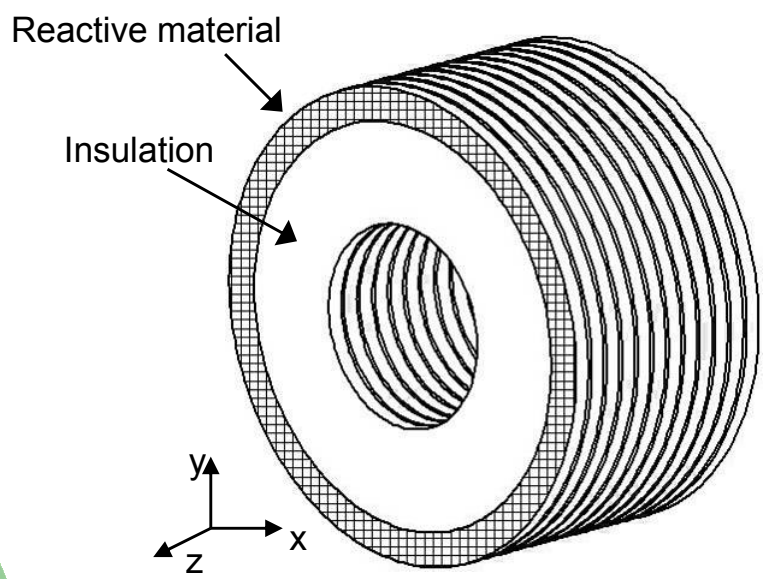
Uses a two step solar-thermochemical process based on a metal-oxide to split water or carbon dioxide:

1) Fe_3O_4 + Heat→ $3FeO + 1/2O_2$

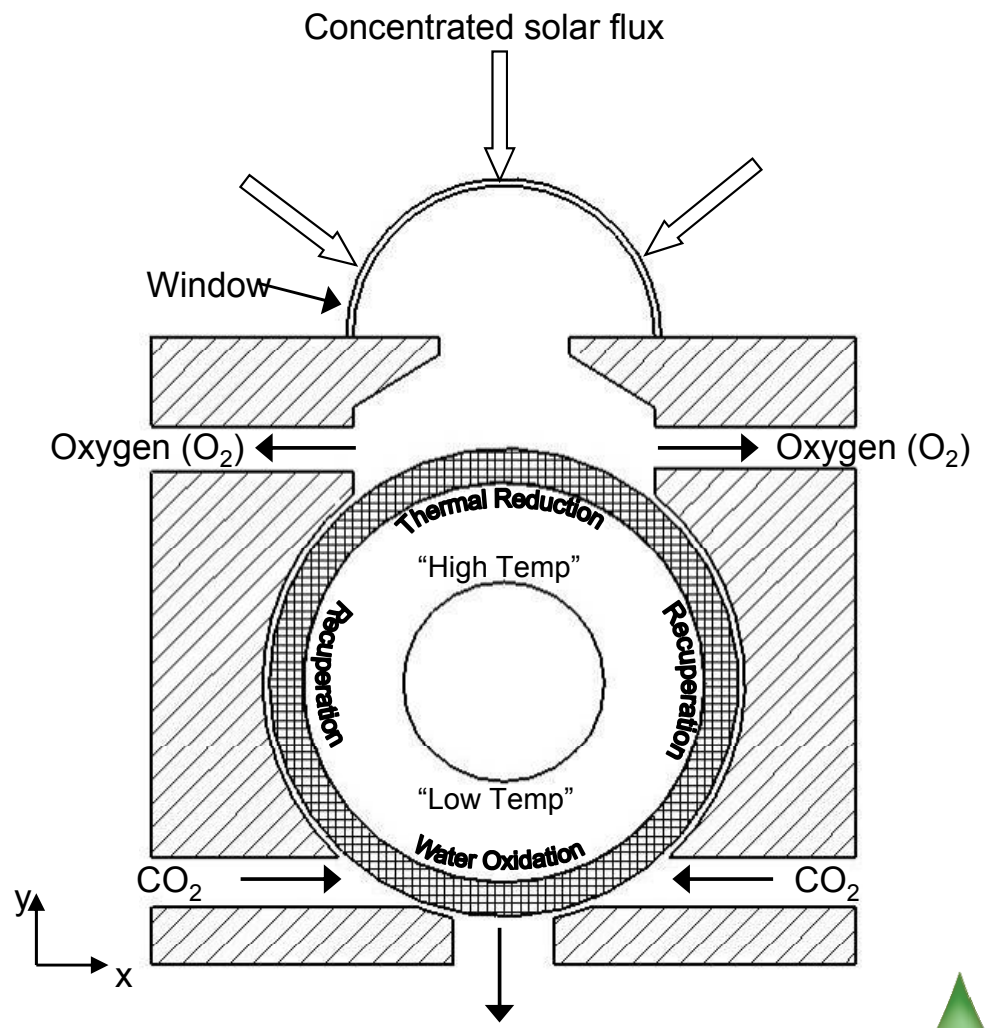
2) $3FeO + CO_2 \rightarrow Fe_3O_4 + CO$

Net: $CO_2 \rightarrow CO + 1/2O_2$

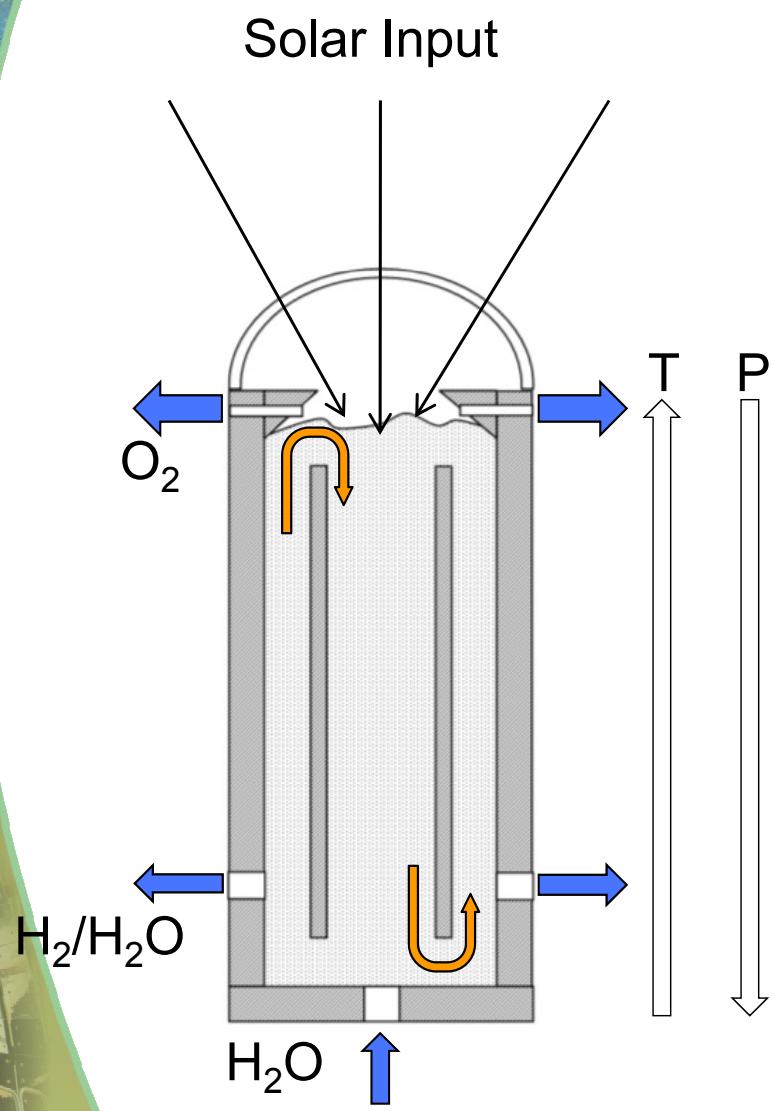
Set of Counter-Rotating Rings



Cross-Section Illustration



Particle Reactor Concept



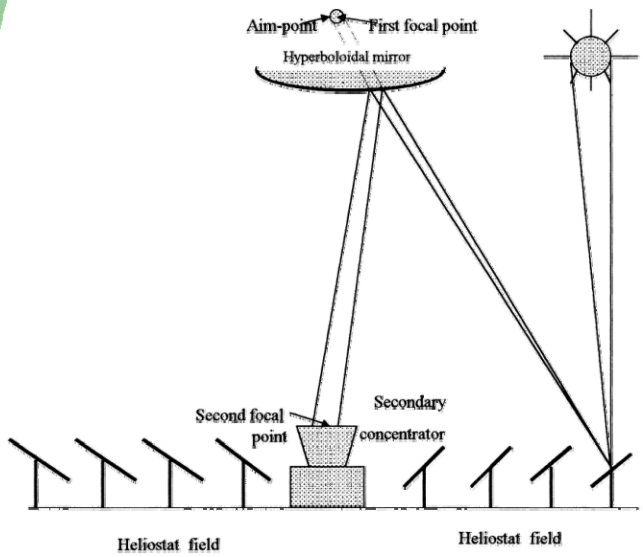
- Possible reaction sequence

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2 \qquad ca.\,1500^{o}C$$

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2 \quad 600-1200^{o}C$$

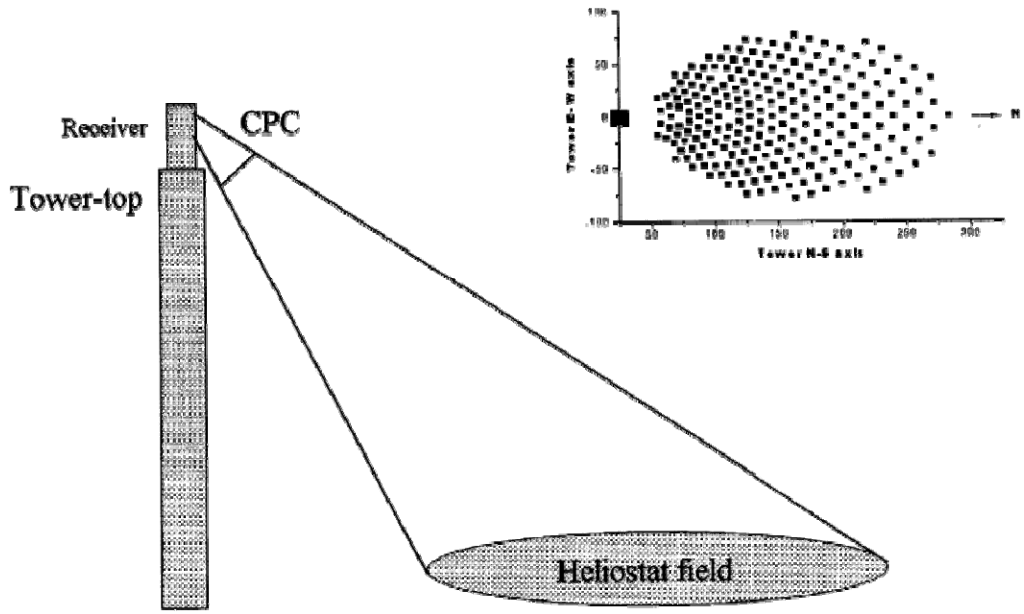
- Can be deployed on parabolic or central receiver
  - Requires beam down optics
- This is the only current reactor concept that includes > four of the "key attributes"

Solar Collection Systems



Beam Down Receiver

From Solar Energy, Segal and Epstein, 1999



Central Receiver

From Solar Energy, Segal and Epstein, 1999

Parabolic Dish

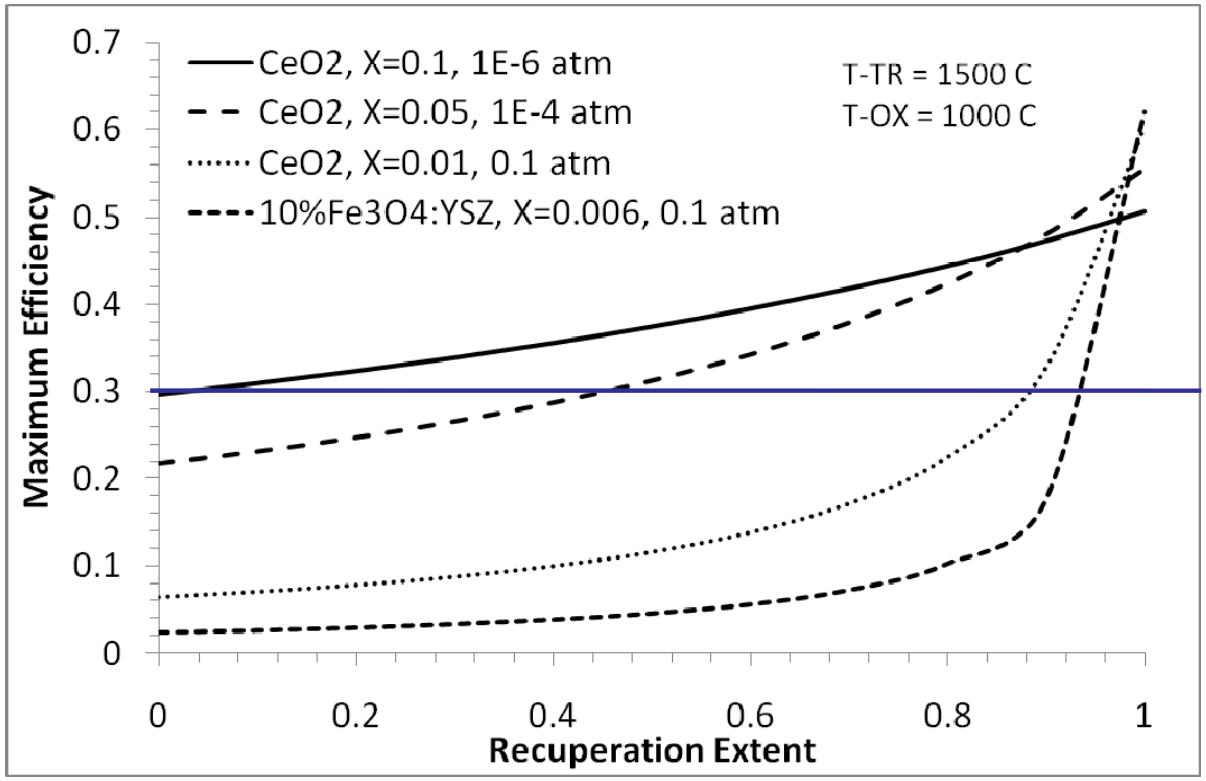
Thermochemical Reactor Summary

Reactor	Continuous Operation	Pressure Separation	Recuperation[1]	Direct Irradiance	Spatial Product Separation[2]	Institute	Ref
CR5	X		X	X	X	SNL	[9], [12]
Moving particle bed	X	X	X	X	X	SNL	-
Rotary reactor	X			X	X	TIT	[8]
Lined cavity		X		X		ETH, CalTech	[6]
Tubular packed bed		X				CU Boulder	[9]
Tubular flow	X[3]	X			X	CU Boulder	[7]
Hydrosol		X		X		DLR	[13]
Fluidized Bed	X			X	X	Univ. Niigata	[14]

[1] Credit for recuperation is given only to those reactors that employ counterflow heat transfer, a necessary criteria for maximizing sensible energy recovery.
[2] This is only possible in reactors with a moving reactive material. All other reactor are batch-type and have temporal product separation. Some downstream processing may still be needed in all cases if excess water or carbon dioxide is used in the oxidation reaction.
[3] This is a batch type concept given that hydrogen and oxygen are not made simultaneously. However, the thermal reduction reaction is run continuously while solar energy is available with the reduced oxide stored for later use.

Reactor Performance

- A good reactor can beat electrolysis with current materials…on paper.
- Reduced pressure looks good, but volumetric flows are huge
- Improving material thermodynamics can pay off - low pressure not required, lower temperature TR

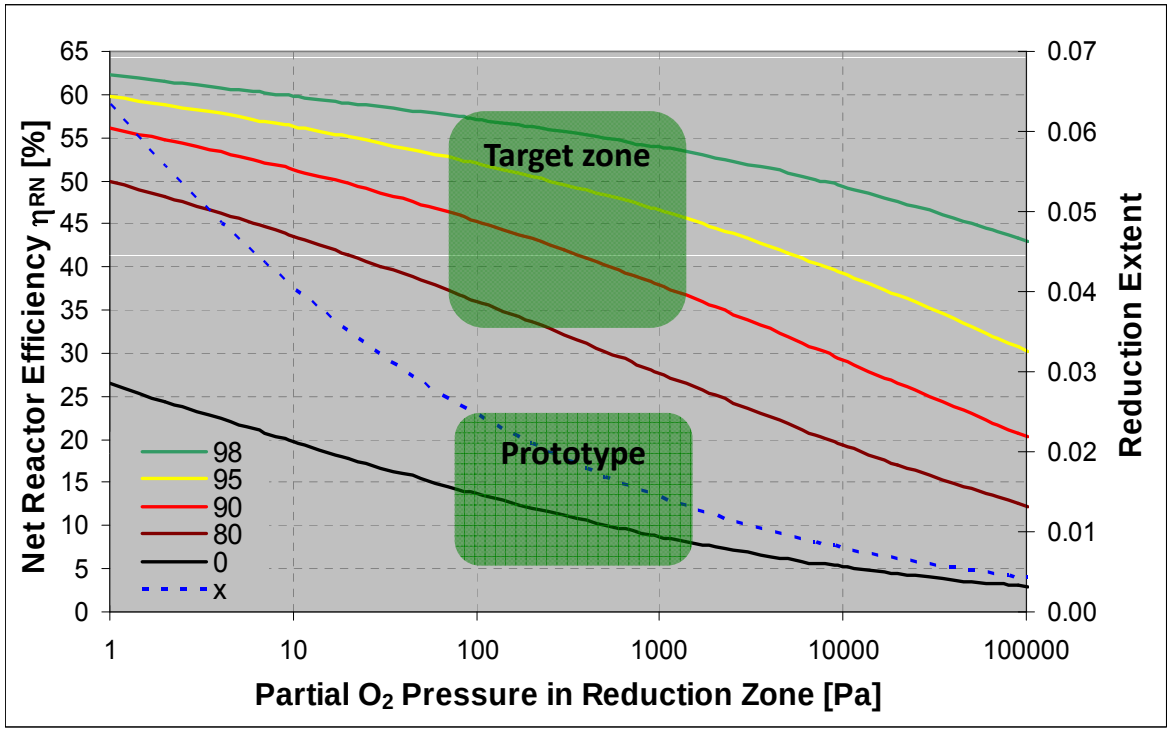


$$Output = HHV_{H2}$$

$$Input = \frac{(1-Eff)*C_{p,reactant}*\Delta T}{\frac{n_{H2}}{n_{reactant}}} + \left(\Delta H_{Reaction} + \frac{RT\ln\frac{p_{atm}}{p}}{\eta_{h-w}}\right) + Q_{H2O}$$

Particle Reactor Performance Map

- Thermal efficiency of > 55% possible with CeO_2 reactant
  - Better reactants = better efficiency
  - More recuperation = better efficiency
- Electrochemical route: heat to hydrogen of 40%*80%=30%

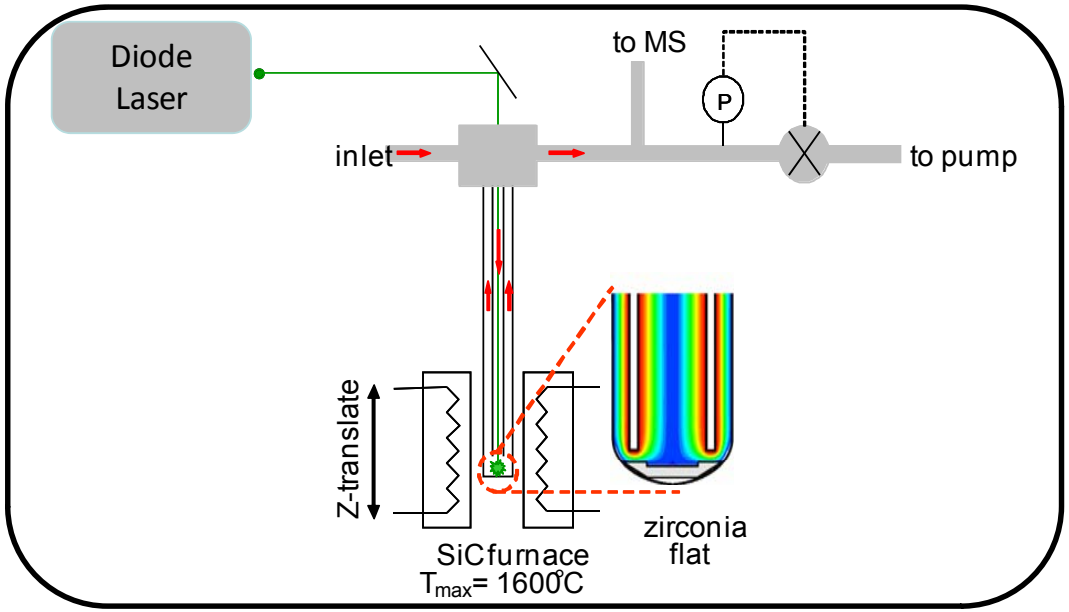


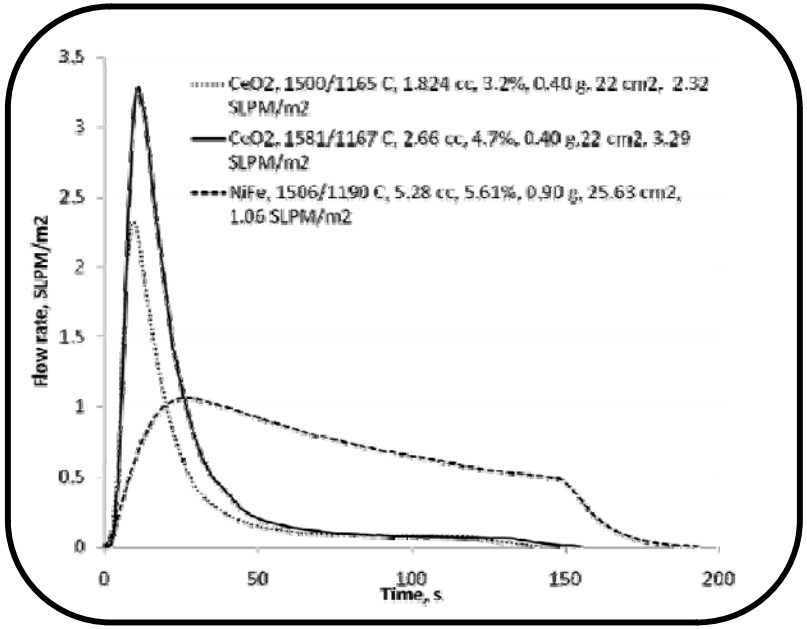
For success, we need great materials <u>and</u> great reactors

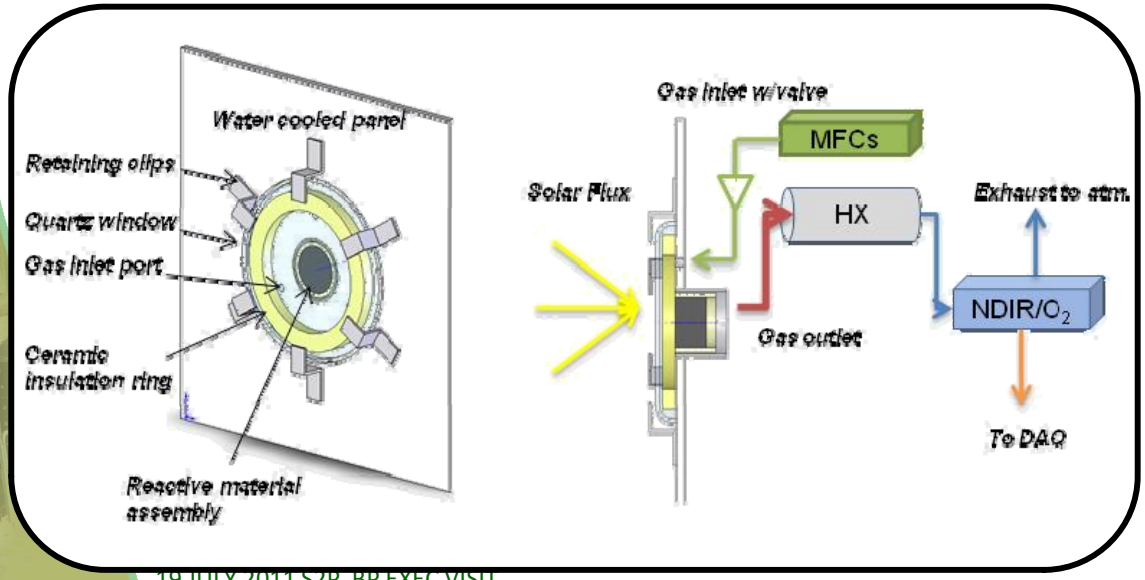
Reduction to Practice

- Some things that “look good on paper” are really difficult to demonstrate
- Technical challenges being addressed are:
  - Reactant performance
  - Material durability
  - Material compatibility

Reactant Performance



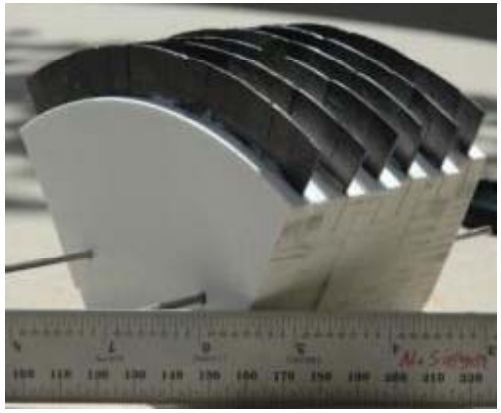




- Thermodynamics
  - High fuel/reactant ratio
- Kinetics
  - Reaction complete <1 min

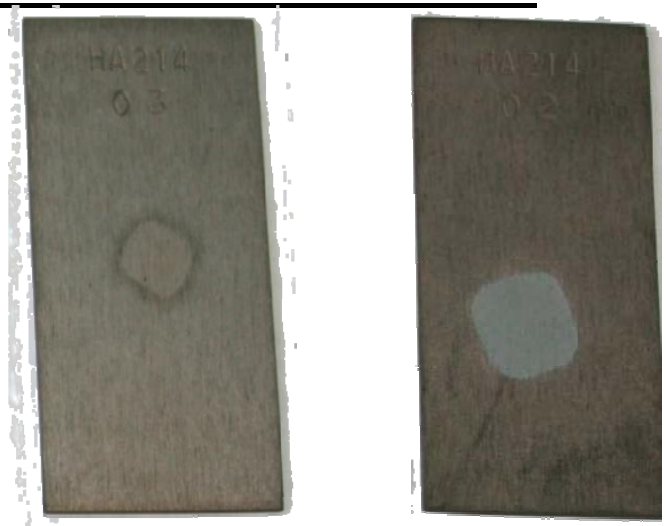
Durability

- Physical and chemical durability are key issues: Survival is the first step toward reaching performance targets
- Monoliths
  - Thermal shock, stress risers, and CTE mismatch
  - Parallel investigations:
    - On-sun testing
    - Thermal cycling in the lab
    - Strength evaluation
  - Need to evaluate fatigue over multiple cycles
- Powders
  - Sintering, abrasion, reaction



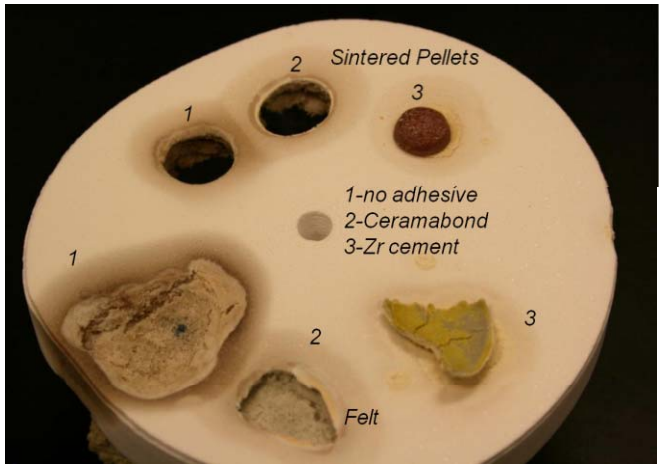
Material Compatibility

- We don't want the reactor and reactants to react…with each other.
- We have investigated the reactivity of ceria with many materials
  - Alumina to 1450°C
  - Haynes 214 to 1400°C
  - SiC to 1400°C
- Material strength is also a concern
  - Creep in metals
  - Shock resistance in ceramics



1200°C 1400°C

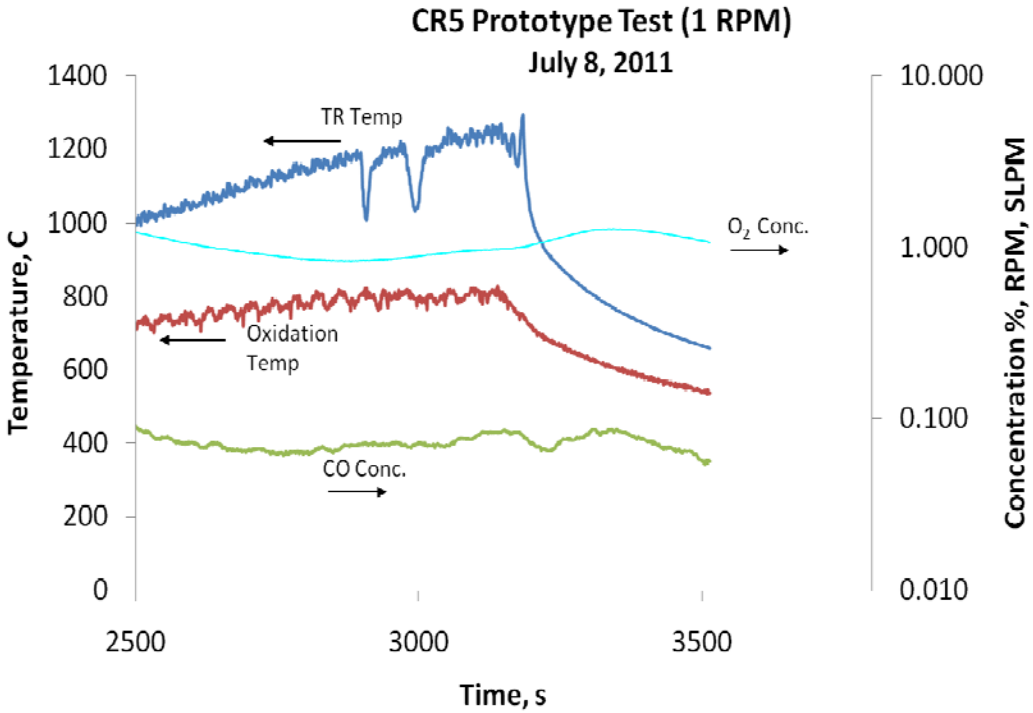
Haynes 214, 10 ppm O_2

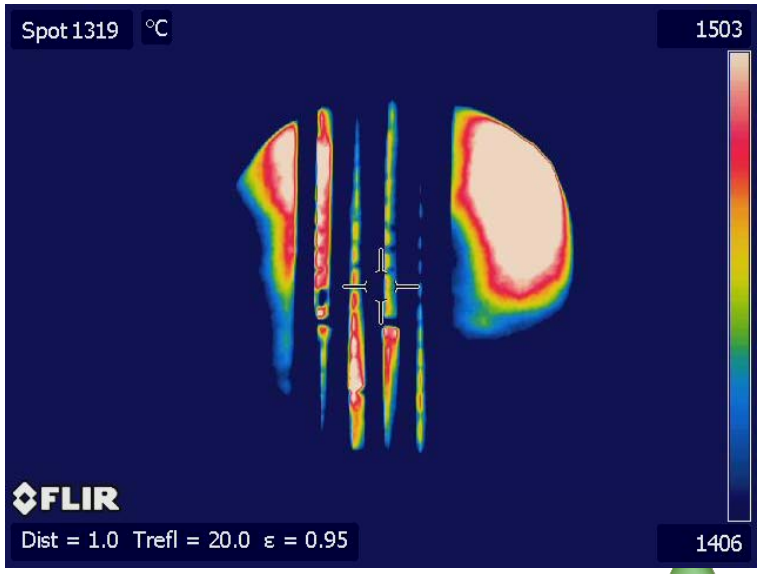


Current Status

CR5 On-Sun Testing

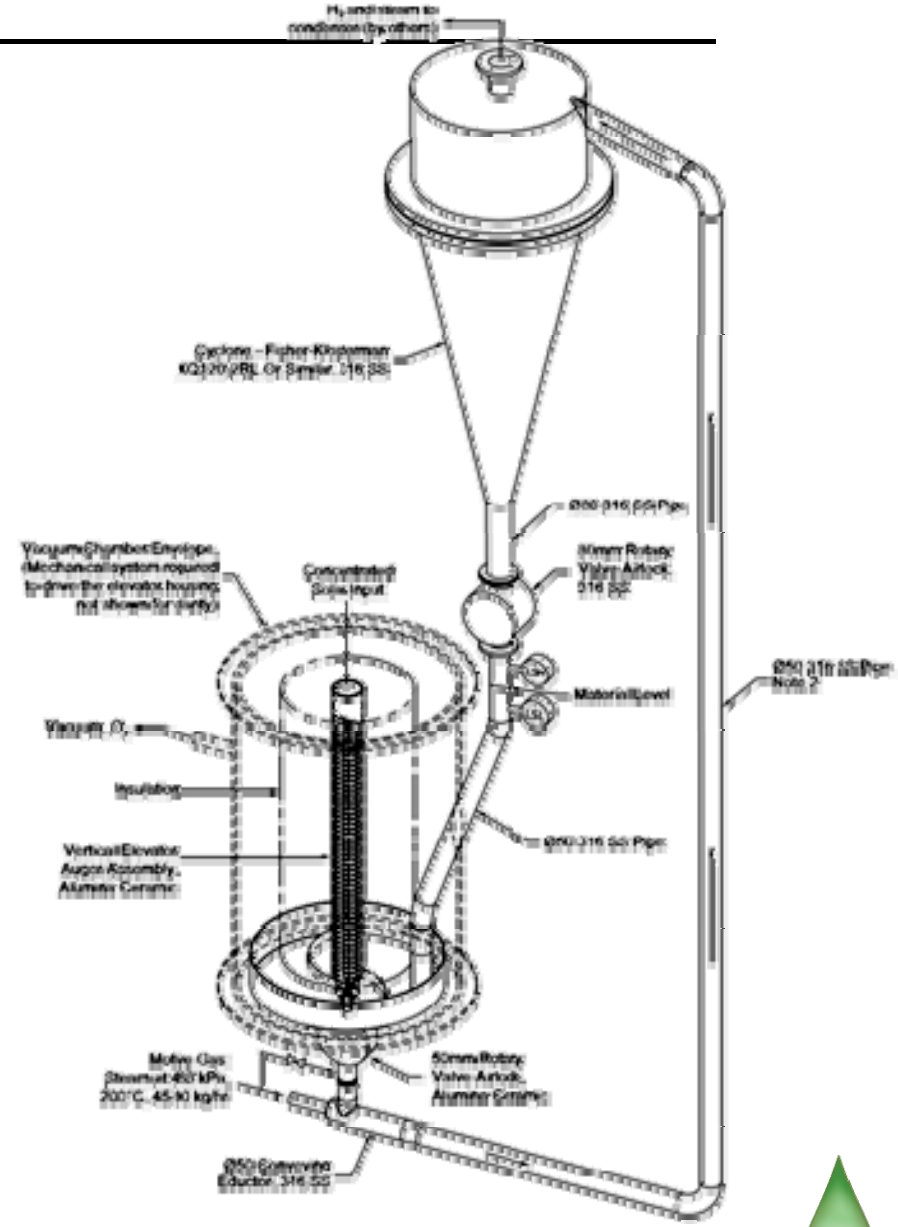
- On-sun testing is ongoing
  - Durability issues are being resolved





Particle Reactor

- 5-10kW$_{th}$ prototype design underway, but limited
- Subcontract with particle flow experts Jenike and Johanson (SLO, CA)
  - First contract successfully completed: baseline design and physical property measurement



Materials

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

- 5% < [H_2O] < 40%
- Variable heating rates
- 10 torr < P < 100 torr
- 800 °C < T_{oxd} < 1200 °C

- Investigating a number of material chemistries
  - Chemical systems
    - $M^{+n}/M^{+(n+1)}$ redox couples
    - $MO_{n-\delta}$ non-stoichiometric oxides
    - "CU hercynite"
    - Thin film form, bulk modified by doping or substitution
  - Supports
    - m-ZrO_2, CeO_2, Al_2O_3

Future Work Plans

The Goal

- To demonstrate a thermochemical fuel production system with the potential to be commercially viable
  - Focus efforts on two-step metal oxide cycles
  - Develop better materials and better reactors

Reactor

- Concept design, evaluation, and selection
  - System design approach at the commercial scale
- Detailed design/build/test of a prototype system
  - Demonstrate all key operating characteristics and subsystems at a meaningful scale
  - Meet critical performance targets:
    - Solar to fuel conversion efficiency – same order as solar electrolysis
    - Durability – maintain performance over several days with multiple thermal cycles

Materials

- **Develop performance metrics for comparing material chemistries**
  - Normalize for inherent material complexities
    - Thin films, powders, engineered forms
  - Account for effects of disparate phenomena
    - Active/accessible loading (morphology, porosity, etc.)
    - reduction and oxidation rates
    - cycle variability/reaction extent (reactor design & intended use)
    - cycle durability
- **Materials discovery**
  - High throughput screening of non-stoichiometric oxides
    - Computational and experimental
  - Novel active material morphologies
    - Nano-structured

Thanks for your attention.

Questions?