Development of Solar-powered Thermochemical Production of Hydrogen from Water

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UNLV Research Foundation
Las Vegas, Nevada

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SOLAR THERMOCHEMICAL HYDROGEN GENERATION PROJECT
Sponsored by U.S. Department of Energy

Project ID No. PD11

Overview

Timeline

- Start: 6-25-2003
- End: 12-31-2007
- Percent complete: 65%

Budget

- Total Project Funding

  $11,118,362 DOE

  $1,886,852 Cost share

- Funds received in FY06

  $3,366,000

Barriers

AU. High-Temperature Thermochemical Technology

AV. High-Temperature Robust Materials

AW. Concentrated Solar Energy Capital Cost

AX. Coupling Concentrated Solar Energy and Thermochemical cycles

Partners

The University of Nevada, Las Vegas   The University of Colorado   Sandia National Laboratories
The National Renewable Energy Laboratory   Argonne National Laboratory General Atomics
ETH-Zurich TIAX, LLC

Objectives

- Identify a cost competitive solar-powered water splitting process for hydrogen production
- Conduct experimental studies to complete quantitative selection
- Numerical and experimental evaluation of solar receiver concepts for integration with thermochemical processes
- Implement consistent methodology for comparing economic viability of cycles

Approach

- Design and implement a thermodynamic and experimental comparative assessment methodology to screen all known thermochemical cycles and select the top several performers
- Carry out critical experimentation to determine the real viability of down-selected cycles
- Develop validated designs for solar collector system components for integrated system analysis
- Analyze cost and efficiency metrics for integrated cycle performance
- Develop demonstration plant concept design(s) for surviving 1 to 3 competitive cycle(s) and demonstrate them at a semi-integrated bench scale, including on-sun testing

Technical accomplishments/ progress/results

- Cycle database, scoring, and initial down-select completed
- Experimental work on 5 cycles targeting cycle closure/viability studies
- CFD modeling for developing understanding of thermal transport in two solar receiver concepts
- Experimental prototypes designed and under construction for aerosol reactor, solid particle receiver, and CR5 ferrite reactor
- Initial cost analysis performed for two leading cycles

Cycle selection and investigation

- 351 unique cycles have been discovered and scored
- 12 cycles found to be worthy of further experimental study
- 5 of those 12 are currently under active study by SHGR

Volatile Metal Oxides

•Zinc oxide

$$ZnO \xrightarrow{1600^\circ C - 1900^\circ C} Zn + \frac{1}{2}O_2$$

$$Zn + H_2O \xrightarrow{300^\circ C - 400^\circ C} ZnO + H_2$$

•Cadmium Carbonate

$$CdO \xrightarrow{1450^\circ C} Cd + \frac{1}{2}O_2$$

$$Cd + CO_2 + H_2O \xrightarrow{120^\circ C} CdCO_3 + H_2$$

$$CdCO_3 \xrightarrow{350^\circ C} CdO + CO_2$$

Non-volatile Metal Oxides

•Sodium manganese

$$Mn_2O_3 \xrightarrow{1500^\circ C} 2MnO + \frac{1}{2}O_2$$

$$MnO + NaOH \xrightarrow{700^\circ C} NaMnO_2 + \frac{1}{2}H_2$$

$$2NaMnO_2 + H_2O \xrightarrow{350^\circ C} 2NaOH + Mn_2O_3$$

•Cobalt ferrite

$$Co_{0.67}Fe_{2.33}O_4 \xrightarrow{1400^\circ C} Co_{0.67}Fe_{2.33}O_{4-\delta} + \frac{\delta}{2}O_2$$

$$Co_{0.67}Fe_{2.33}O_{4-\delta} + \delta H_2O \xrightarrow{1000^\circ C} Co_{0.67}Fe_{2.33}O_4 + \delta H_2$$

Other

•Hybrid copper chloride

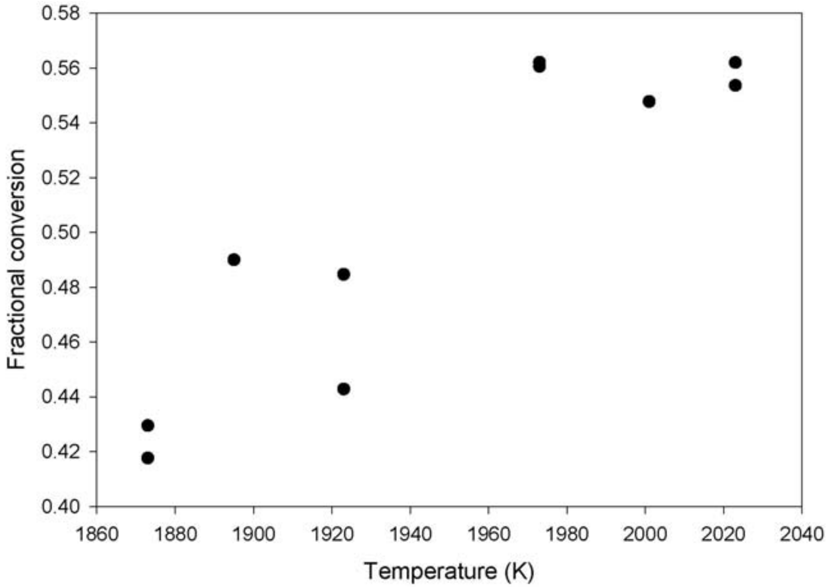
$$Cu_2OCl_2 \longrightarrow 2CuCl(l) + \frac{1}{2}O_2$$

$$2Cu + 2HCl(g) \longrightarrow H_2(g) + 2CuCl(l)$$

$$4CuCl \longrightarrow 2Cu + 2CuCl_2$$

$$2CuCl_2 + H_2O \longrightarrow Cu_2OCl_2 + 2HCl$$

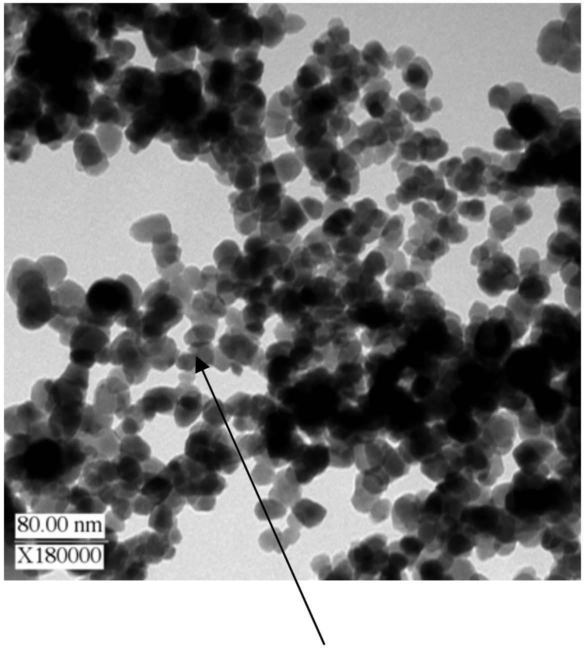
Aerosol Dissociation of ZnO



- Forward conversions > 55% in less than 1s residence time
- Net conversions ~40% - highest ever achieved
- Aerosol rates 3-4 orders of magnitude greater than stationary configurations
- Rapid quench mitigates recombination

- 9 cm ID x 117 cm Al_2O_3 tube

$$ZnO \longrightarrow Zn + \frac{1}{2} O_2$$



- Extremely small product particles (>50 nm) give fast rates in H_2 generation step

Aerosol processing can give fast rates for many high temperature cycles

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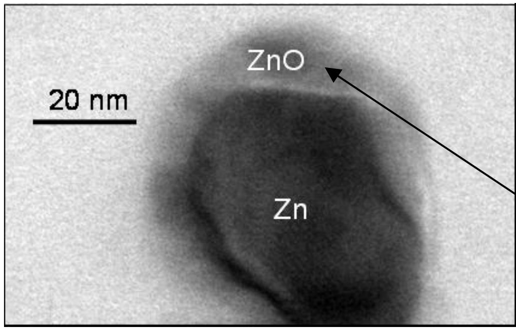
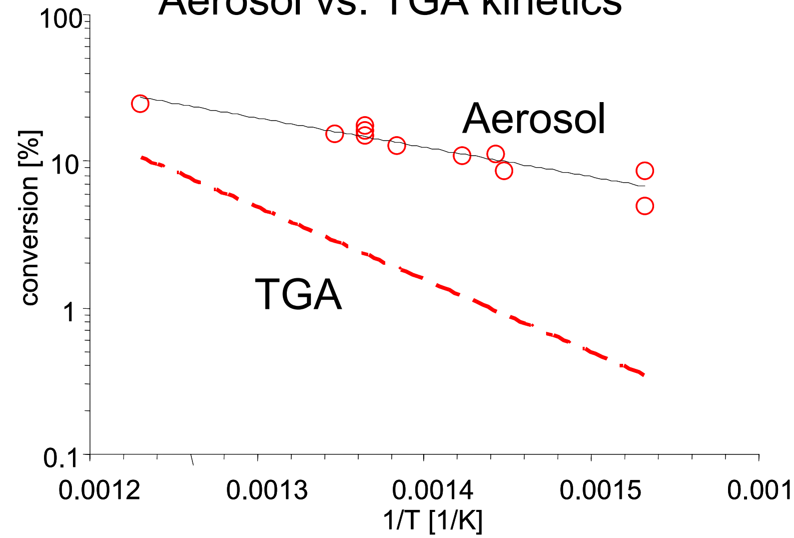
Production of hydrogen from Zn/H_2O



Passivating ZnO film

Reacted particle

Nano-size Zinc Conversion (<1 sec)
Aerosol vs. TGA kinetics



Aerosol Kinetics >> TGA Kinetics

- Successful generation of hydrogen
- Reaction is mass transfer limited – small particles are better
- Aerosol rates much faster than stationary configurations

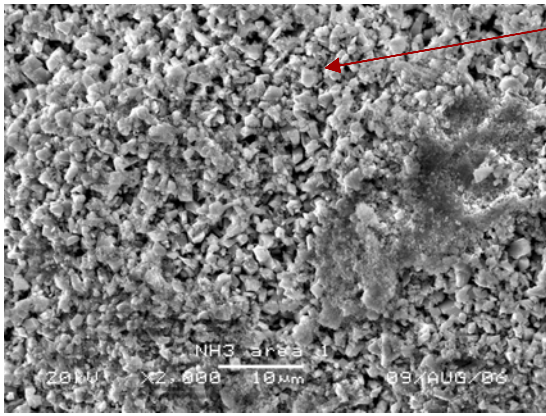
On-sun cycle testing in progress at High Flux Solar Furnace (NREL)

Hydrogen production from Cd/H_2O

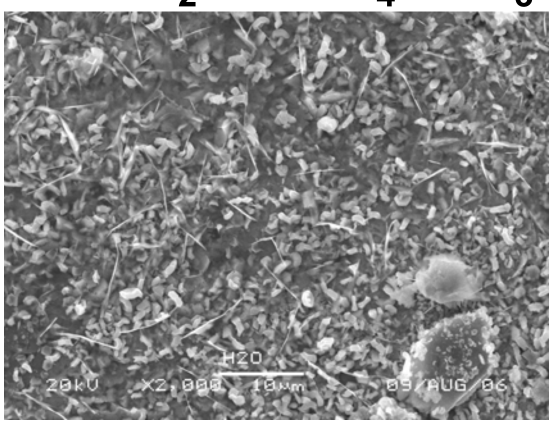
$$Cd + CO_2 + H_2O \longrightarrow CdCO_3 + H_2$$

- H_2 production a strong function of available Cd surface

$CdCO_3$ crystals



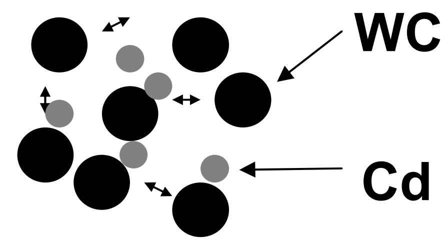
Cd + H_2O + NH_4HCO_3



Cd + H_2O

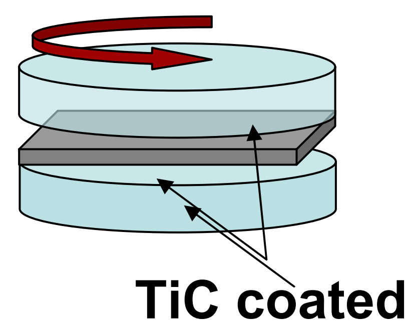
- $Cd(OH)_2$ forms passivating layer on Cd
- $CdCO_3$ present as porous crystals
- Attrition can open more Cd surface to reaction, speed H_2 generation rates
- Rates have been increased to 5% total conversion/hr

Ball milling



Conversion: 4%/hr

Grinding



5%/hr

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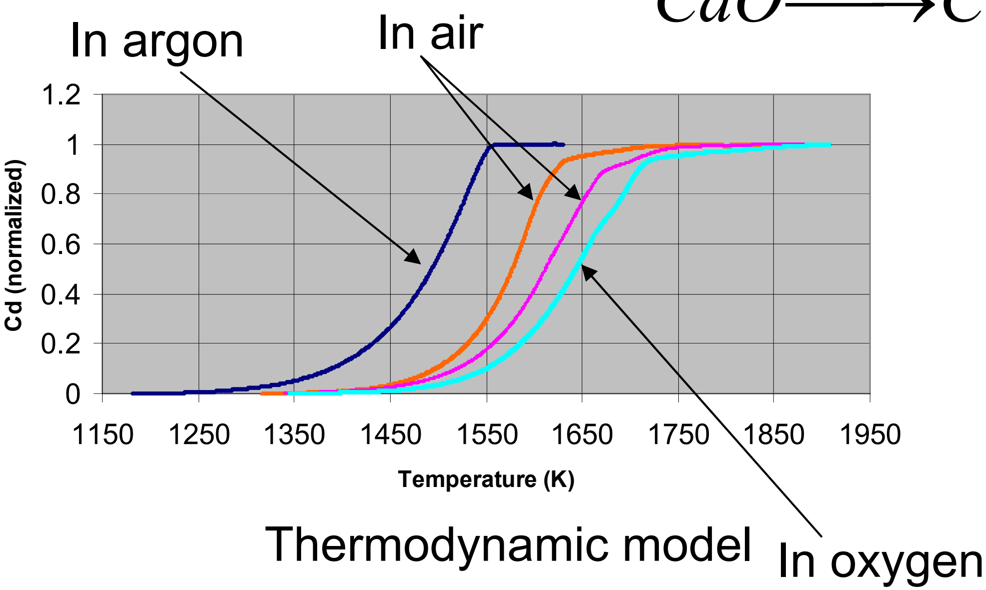
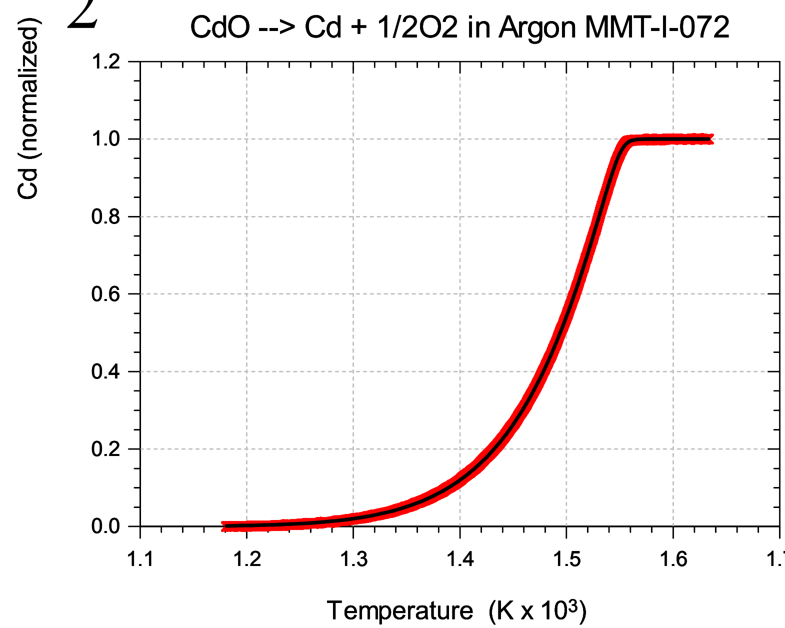
Kinetic model for CdO decomposition

$$CdO \longrightarrow Cd + \frac{1}{2}O_2$$



Thermodynamic model



Kinetic analysis in TGA

$$\frac{dX}{dt} = k_0 e^{\frac{-E_a}{RT}} (1 - X)^n$$

In argon: E_a=269.4 kJ/mol , k_0=1.36 X 10^9 s^{-1}

In air: E_a=470.9 kJ/mol , k_0=2.57 X 10^{15} s^{-1}

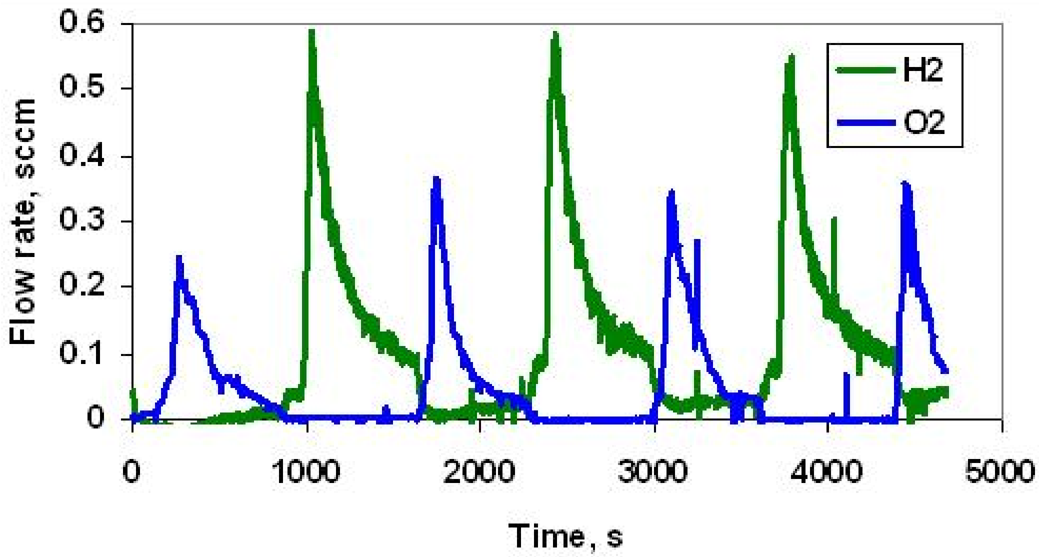
In oxygen: E_a=438.9 kJ/mol , k_0=6.39 X 10^{13} s^{-1}

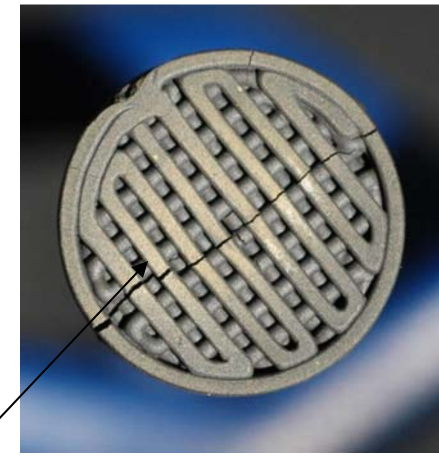
- Presence of oxygen strongly affects CdO decomposition temperature
- Kinetics confirm thermodynamic predictions
- Reaction should be operated in inert to mitigate recombination, speed rates
- Work continues on investigation of recombination reaction

Solar Ferrite Cycle Closure Demonstrated

$$Co_{0.67}Fe_{2.33}O_4 \xrightarrow{1400\,^{\circ}C} Co_{0.67}Fe_{2.33}O_{4-\delta} + \frac{\delta}{2}O_2$$

$$Co_{0.67}Fe_{2.33}O_{4-\delta} + \delta H_2O \xrightarrow{1000\,^{\circ}C} Co_{0.67}Fe_{2.33}O_4 + \delta H_2$$





Before reaction

Ferrite monoliths

After 30 cycles

- On-sun reduction at 1550 °C, H_2 production at 1100 °C
- YSZ-stabilized ferrite shows stability, repeatability
- First cycle closed “on-sun”

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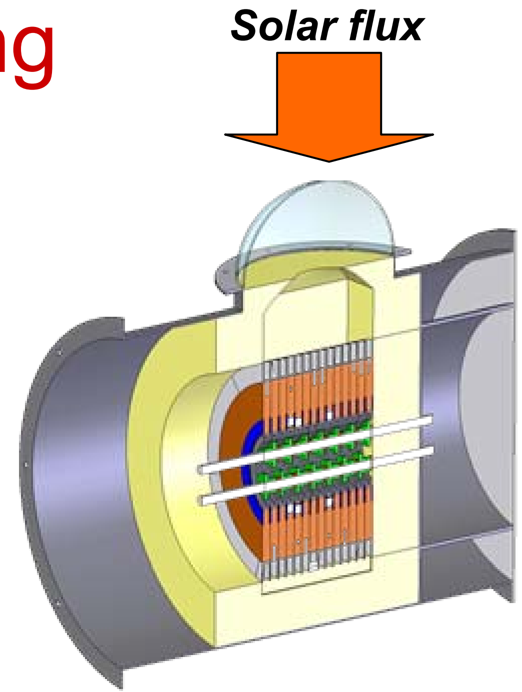
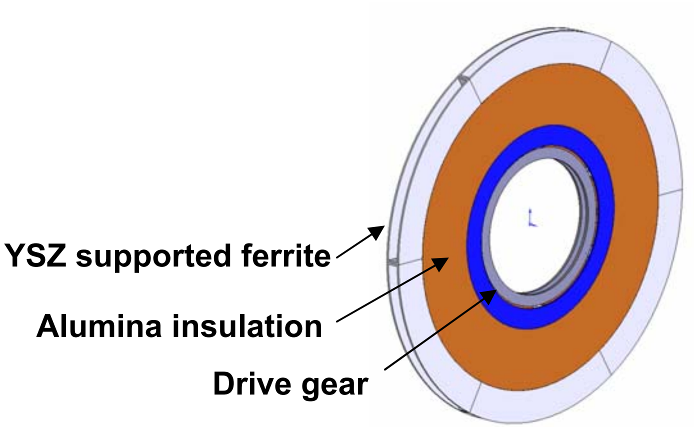
CR5 ferrite reactor constructed and ready for on-sun testing

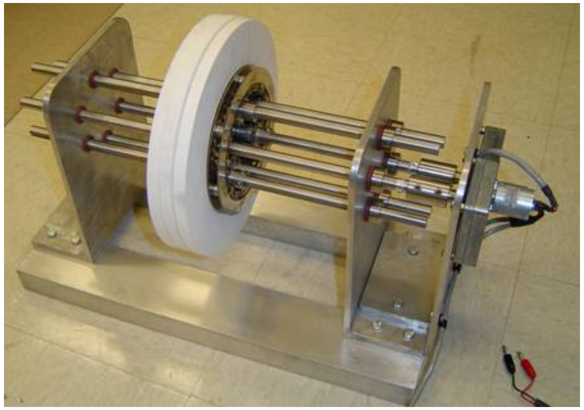
- The prototype CR5 device will operate at a solar input of 9kW
- A set of 14 counter-rotating disks contain about 1.5 kg or ferrite material
- Hydrogen production goal of > 100 slph H2 in August of 2007



CR5 Cross Section



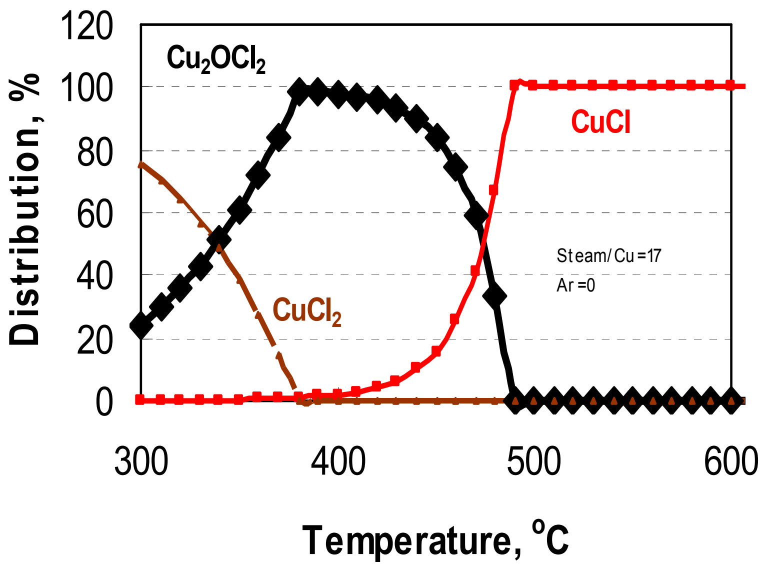
CR5 Rotating Ring



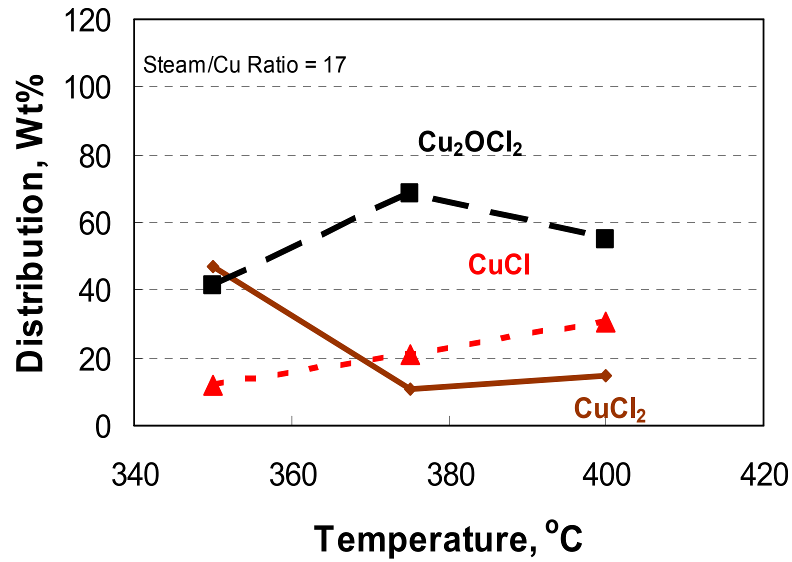
CR5 Drivetrain with Three Rings

Successful reaction of $CuCl_2$

$$2CuCl_2 + H_2O \longrightarrow Cu_2OCl_2 + 2HCl$$



Thermodynamic prediction



Experimental results

- Thermodynamics predict 98% yield of desired Cu_2OCl_2 at 375°C and no significant CuCl formation with steam to copper molar ratio of 17

- Experiments show up to 85% Cu_2OCl_2 production
- Significant amounts of CuCl produced – needs to be mitigated

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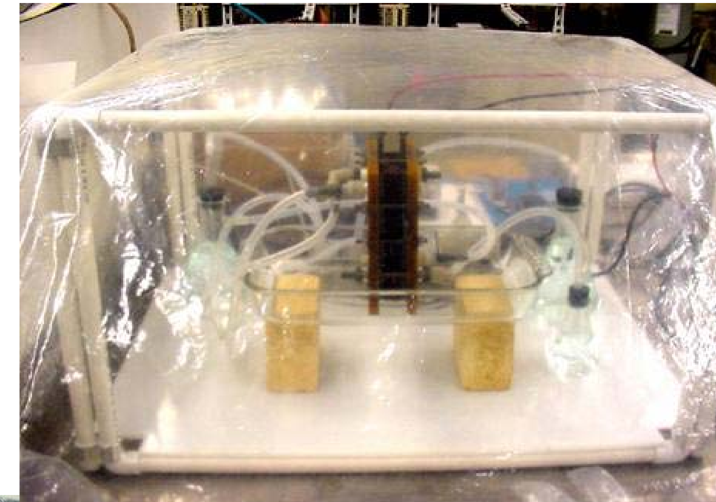
New design for electrochemical cell

- Electrochemical reaction:

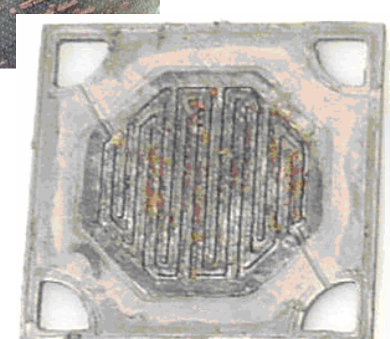
$$CuCl \longrightarrow Cu + CuCl_2$$

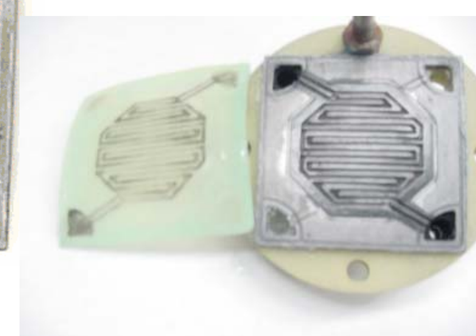
- Original design:
  - Electrochemical flow cell using graphite resistant graphite plates
  - Corrosive $CuCl_2$ caused Cu deposition and membrane destruction
- New design:
  - Plastic frame with graphite channels
  - Work focused on improving cation exchange, reducing shunt current



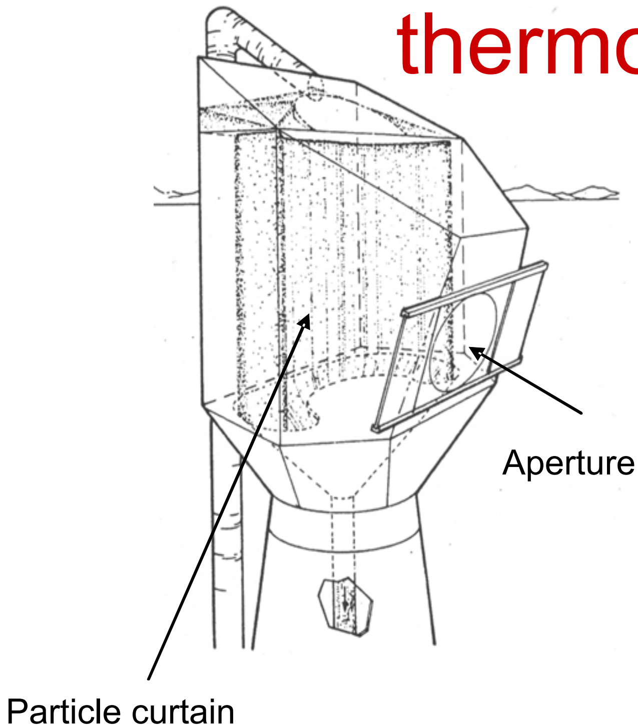
6 months ago

Today





Solid particle advanced solar receiver for thermochemical processes



- Can achieve temperatures in excess of 950 °C
- Falling particles directly heated by solar radiation
- Two-storage tanks and heat exchanger couple to thermochemical process

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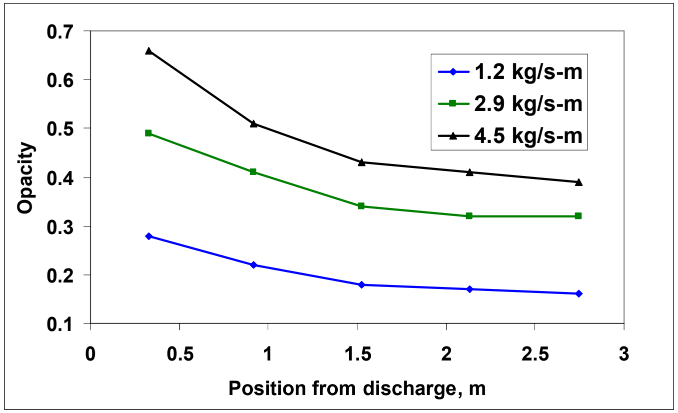
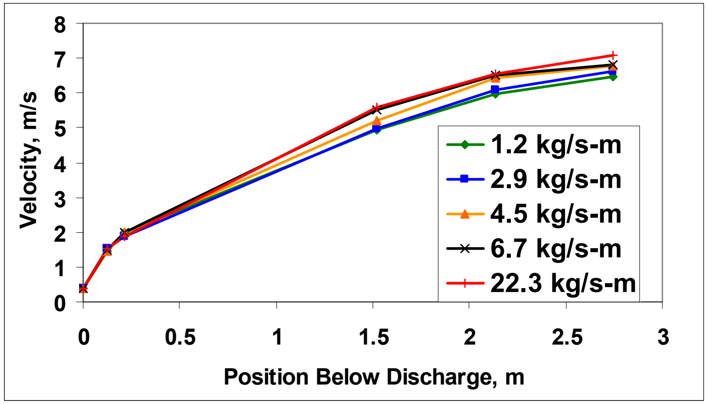
Cold flow testing completed



Increasing the mass flow rate increases the overall curtain opacity and receiver efficiency



Particle velocity affects receiver residence time and particle temperature

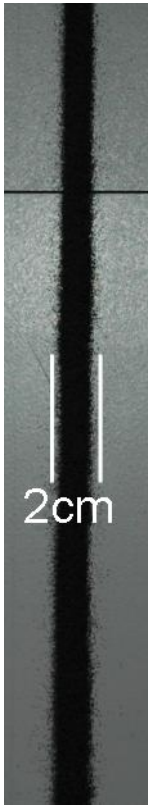
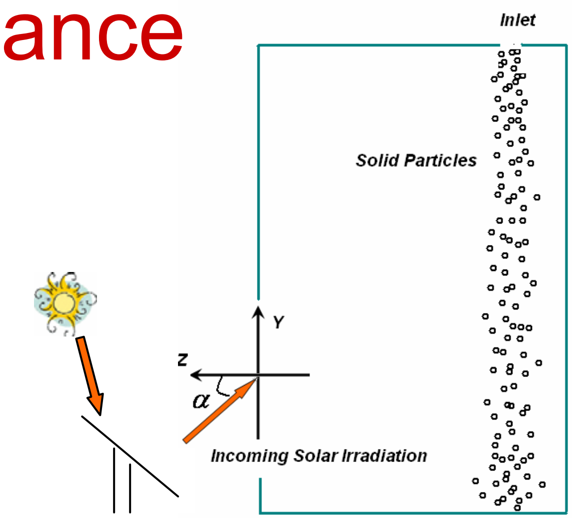
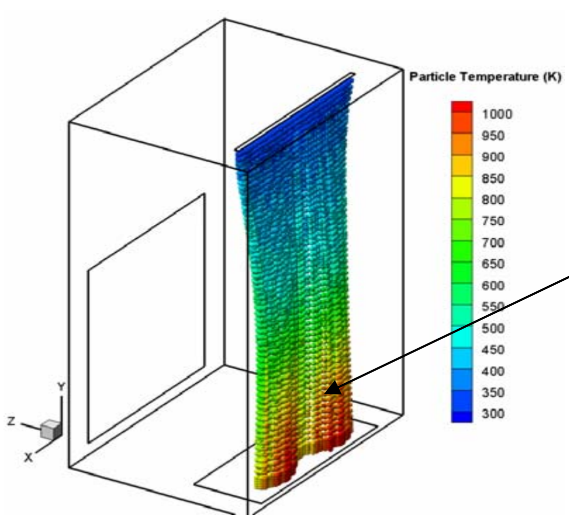


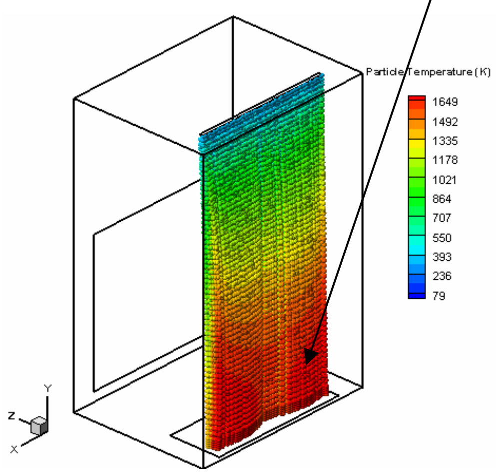
Image taken on side showing curtain thickness

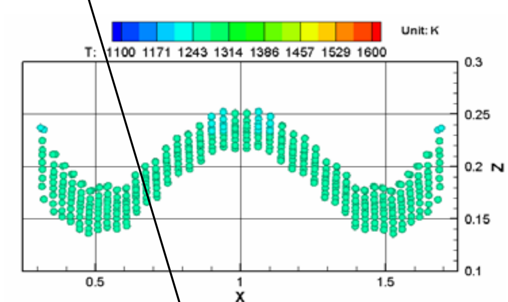
Numerical modeling performed to optimize particle receiver performance



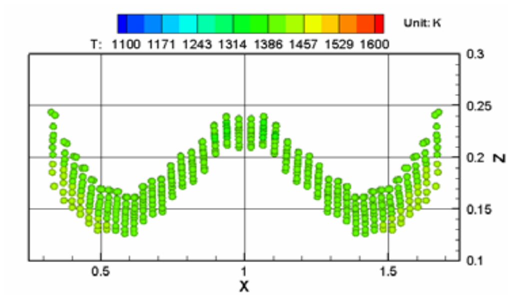
- Small particles give high temperatures, but unstable curtain
- Polydisperse particles give stable, high temperature curtain
- Highest temperatures for incidence angle of 30°



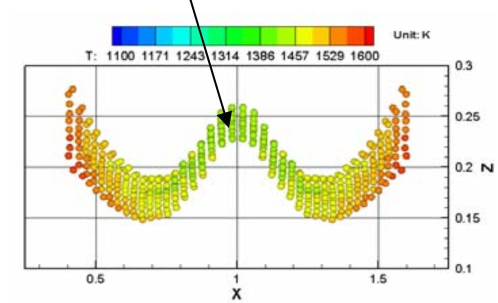




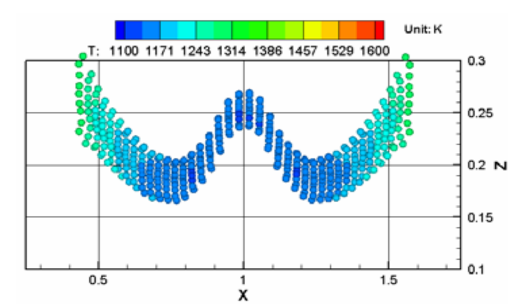
$\alpha = 45^o$



$\alpha = 30^o$



$\alpha = -30^o$



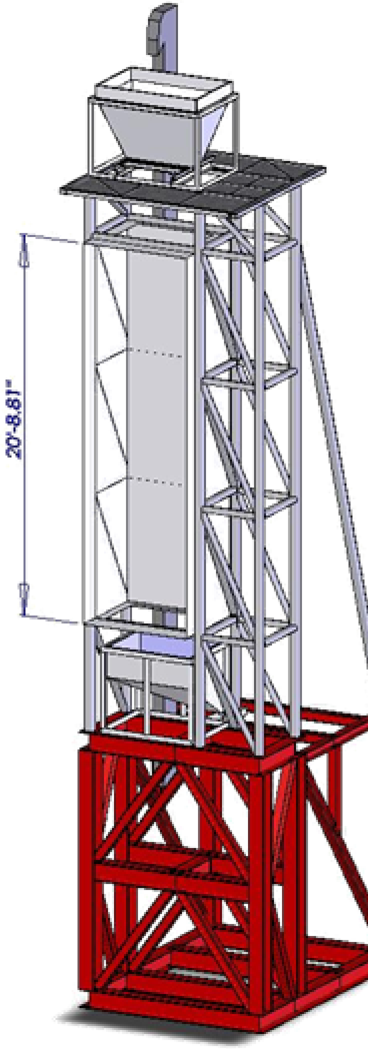
$\alpha = -45^o$

Solid Particle Receiver Design and Construction

- The design and load analysis for the 1MWth Solid Particle Receiver (SPR) has been completed.
- Construction activities have begun
- Testing on-sun at the National Solar Thermal Test Facility (NSTTF) is set for Oct. 2007.

SPR will be tested on top of the power tower

National Solar Thermal Test Facility (NSTTF) at Sandia National Labs



Solid particle receiver prototype test platform

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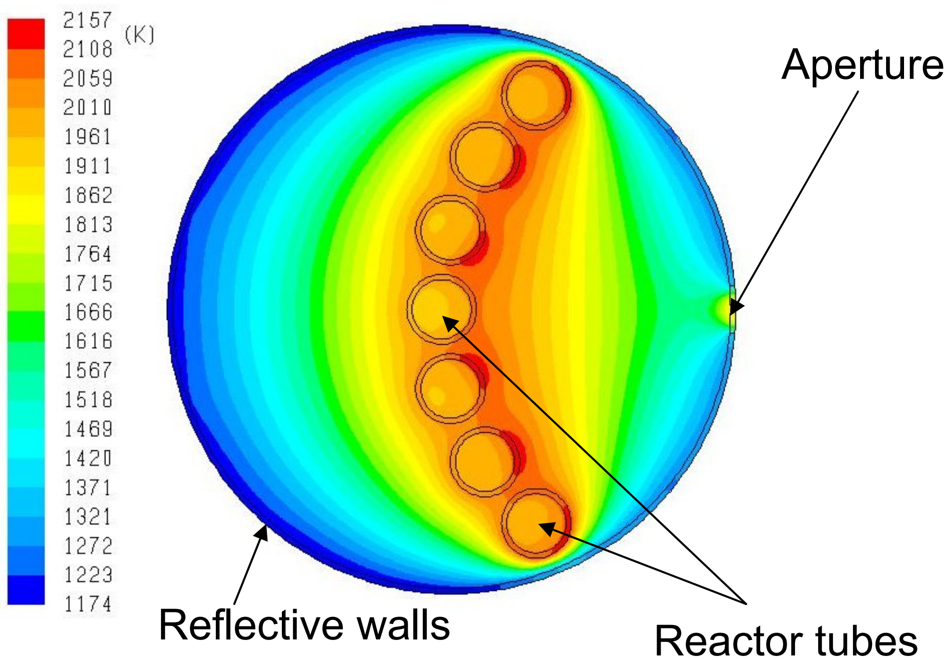
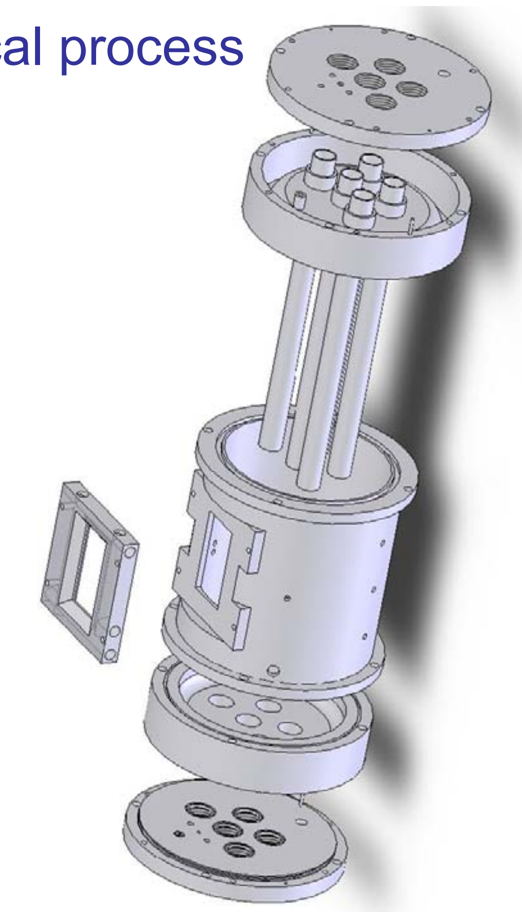
Advanced solar chemical receiver/reactor design

- Design for operation of volatile and non-volatile metal oxide cycles
- Can efficiently transfer solar energy to thermochemical process



Multi-tube design gives high (>36%) receiver efficiency



•5-tube reactor under construction
•Testing at NREL August 2007

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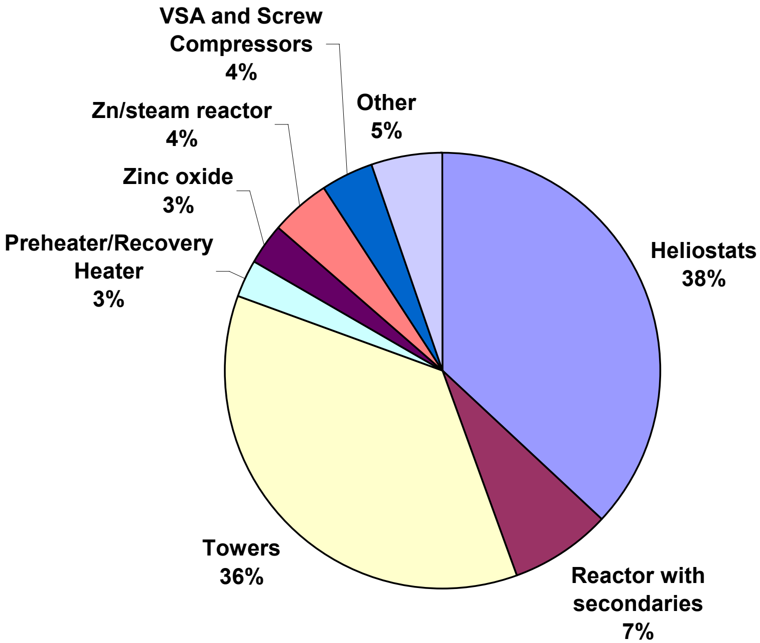
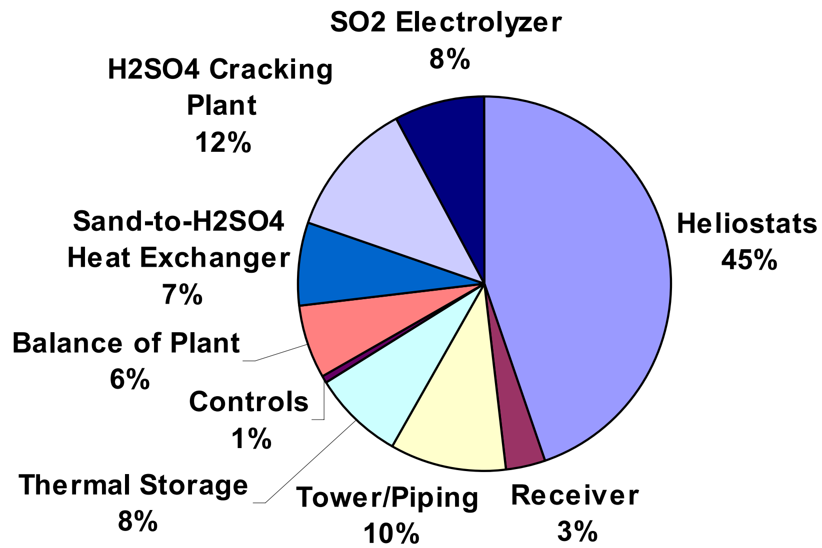
Economic evaluation of thermochemical processes

- Use H2A framework to develop consistent evaluation technique
- 2 processes examined: Zn/ZnO and Hybrid Sulfur
- Central production, 100,000 kg H_2 /day

ZnO/Zn - 2025



HyS - 2025



Zn/ZnO: H_2 costs between $3.10 and $4.85/kg

HyS: H_2 costs between $2.50 and $3.15/kg

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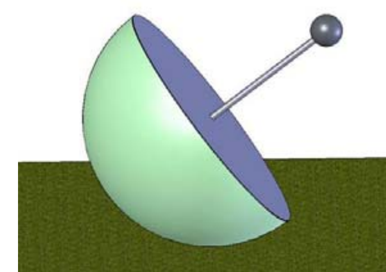
Heliostat Cost Reduction Study

- Heliostats contribute ~50% to the cost of solar H_2 plant
- Two workshops were held to brainstorm ideas for heliostat cost reduction
  - 30 international experts in heliostats and manufacturing
  - ~40% cost reduction possible through significant R&D
- Advanced heliostat design and manufacturing development can enable <$3/kg solar H_2 production
- SAND report will soon be published

TODAY → **FUTURE POSSIBILITIES**



Future Work

- Complete closure of 5 experimental cycles to determine technical feasibility and down-select
- Demonstrate “on-sun” CR5 ferrite reactor, solid particle receiver, and cavity aerosol receiver
- Demonstrate integrated cycle operations “on-sun”
- Continue materials research for implementation in solar receiver and other system components
- Down-select cycles through H2A evaluation of economic performance

Summary

- ***Objective***: Evaluate solar thermochemical water-splitting routes to hydrogen production
- ***Approach***: Screen cycles based on technical criteria, experimentally investigate most promising cycles, develop schemes for solar integration, evaluate economic viability of cycles
- ***Technical accomplishments/progress:*** Completed scoring process, demonstration of all reactions in 5 selected cycles, determination of kinetic/limiting factors in each cycle, design and modeling of three advanced reactor concepts, development of economic methodology for evaluating cycles
- ***Future work:*** Integrated closure of down-selected cycles, “on-sun” operation of advanced reactor concepts, exploration of materials challenges for solar implementation