SAND2008-3332C

DOE Hydrogen Program

Development of Solar Powered Thermochemical Production of Hydrogen from Water

Presented by Nathan Siegel for the Solar Thermochemical Hydrogen (STCH) Team

DOE Annual Merit Review

Washington, DC

June 10th, 2008

Argonne National Laboratory · Colorado University of Colorado at Boulder · NREL · General Atomics · UNLV University of Nevada Las Vegas · TIAX · Sandia National Laboratories

STCH Project Overview

Timeline

Begin: 6-25-2003
End: 9-30-2009
Percent Complete: 75%

Budget

Total DOE Funds:$13.1M
Total Cost Share: $2.2M
FY07-08 DOE: $2M
FY07-08 Cost Share: $300K

Team Members

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

Barriers Addressed

U. High-Temperature Thermochemical Technology
V. High-Temperature Robust Materials
W. Concentrated Solar Energy Capital Cost
X. Coupling Concentrated Solar Energy and Thermochemical cycles

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Project Objectives

Overall

- ***Select one or two cost competitive solar powered hydrogen production cycles for large scale demonstration***
  - Develop solar receiver concepts
  - Perform experimental validations of the key components of prospective cycles
  - Produce economic models of all prospective cycles using a common methodology and assumptions

Metric	Unit	*2008 Target*	2012 Target	2017 Target
Solar Thermochemical Hydrogen Cost	$/kg H_2	*10.00*	6.00	3.00
Heliostat Capital Cost	$/m^2	*180*	140	80
Process Energy Efficiency	%	*25*	30	>35

Milestones and Technical Accomplishments

- **Five prospective cycles (classes) remain in consideration**
- **Cadmium cycle hydrolysis step has been evaluated**
- **Cu-Cl conceptual process design is complete, hydrolysis step demonstrated**
- **Initial experimental evaluation of the solid particle receiver is complete**
- **Solar receiver/reactor concepts are being designed/demonstrated**
- **H2A economic analysis has begun for all cycles.**

- **Go/No Go: A final downselect to 1-2 cycles will be completed by Sept. 1, 2008; alternate cycles might be continued at lower levels of funding**

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Technical Approach

- **The STCH project is divided into five technical task areas**

Task 1: Cycle Feasibility

- Ferrite (CU, SNL)
- Zinc Oxide (CU, ETH)
- Cadmium Oxide (GA, UNLV)
- Manganese Oxide (CU)
- Copper Chloride (ANL)

Task 2: Receiver Studies

- Solid Particle (SNL, UNLV)
- CR5 (SNL)
- Cavity/Aerosol (NREL, CU, ETH)
- Rotary Kiln (ETH)
- Beam Down (GA)

Task 3: Systems

- Ultra-High Temp (SNL, CU, ETH)
- High Temp (SNL, UNLV, ANL)

Task 4: H2A

- Integration of economic analyses (TIAX)

Task 5: Integration -Outreach

- IEA collaboration (SNL)
- Heliostat R&D (SNL)

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Cycle Feasibility Studies

Top Solar Thermochemical Cycles

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 Oxide

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

$$Cd + H_2O \xrightarrow{375\text{–}450^{\circ}C} CdO + H_2$$

Non-volatile Metal Oxides

•Sodium manganese

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

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

$$2NaMnO_2 + H_2O \xrightarrow{850\,^{\circ}C} 2NaOH + Mn_2O_3$$

•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

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

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

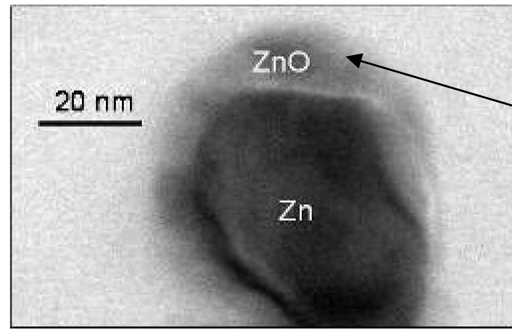
$$4CuCl \longrightarrow 2Cu + 2CuCl_2$$

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

- ***Hybrid Sulfur (HyS) and Sulfur Iodine (SI) are also considered but not actively researched by STCH***

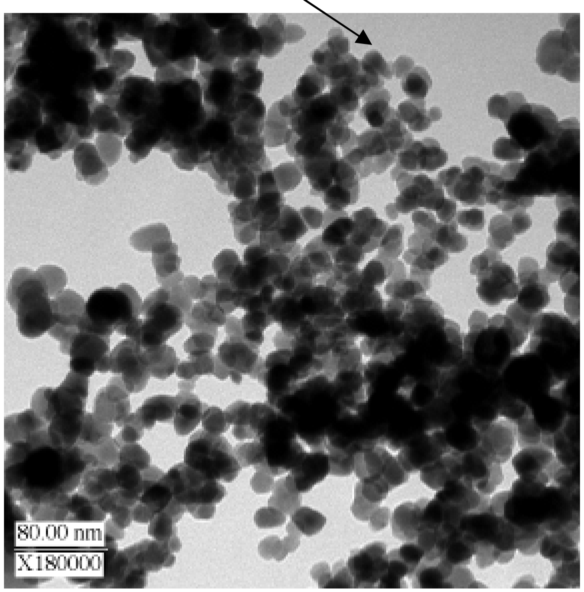
Progress in the Zn/ZnO Cycle

- **Demonstrated highest net conversion (>40%) on record**
- **Future fluidized bed dispersion experiments should lead to >70% conversion, based on Mn_2O_3 results**
- **Extremely small product particles (>50 nm) give fast rates in H2 generation step**

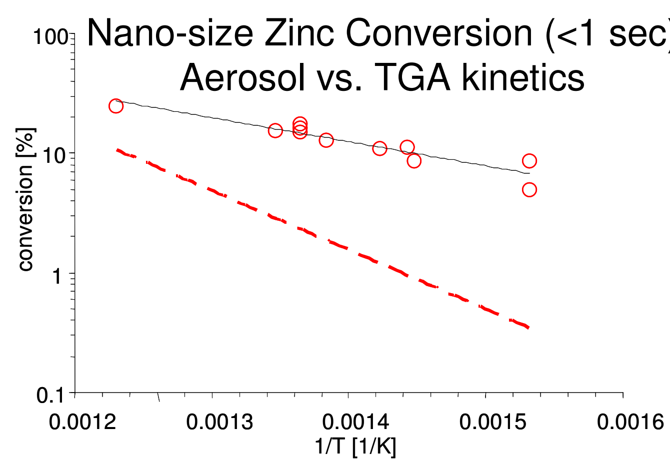


Passivating ZnO film

- **ZnO film growth slows hydrolysis rate – smaller particles are better**
- **Experiments underway at high pressure**
  - **Drive diffusion through ZnO film**
  - **Substitute water pump for H_2 compressor, lower capital costs**

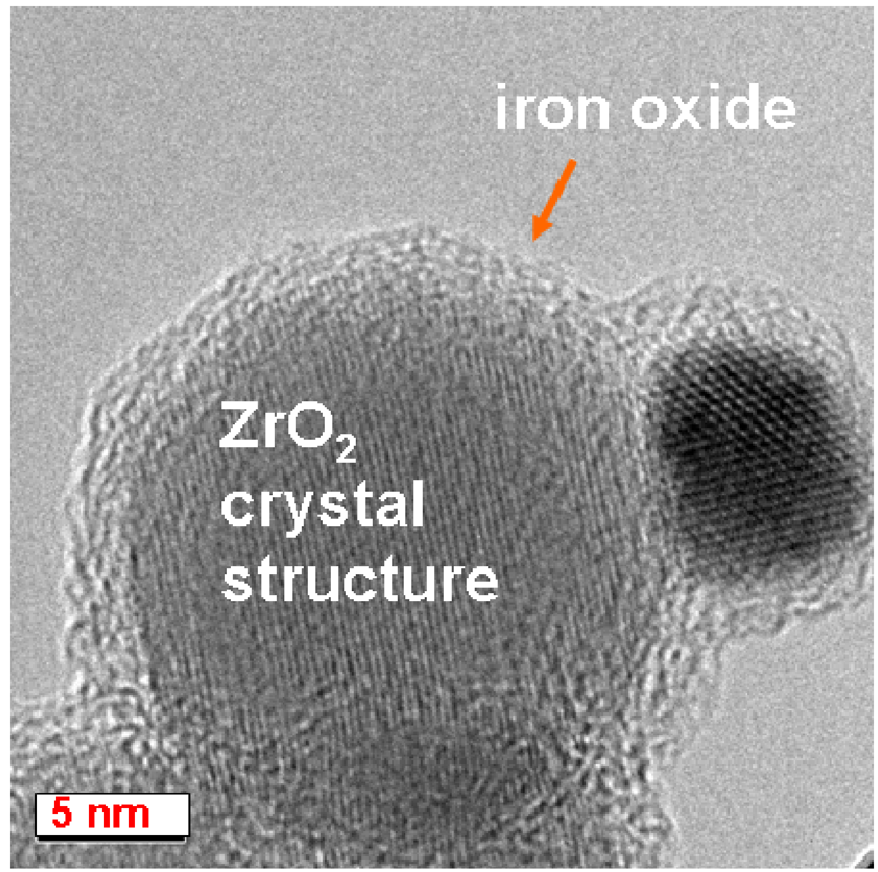


Aerosol processing can give fast rates for many high temperature cycles



Atomic Layer Deposition (ALD) of $Co_xFe_{3-x}O_4$

- *Use ALD as a means to study factors affecting the cycle in order to engineer ferrites more effectively*
  - Ferrite chemistry is not well understood
  - Hydrolysis kinetics are slow
  - Amount of O_2 evolved per mole ferrite affects cycle efficiency
- *ALD offers precise control of*
  - Stoichiometry
  - Film thickness
  - Specific surface area



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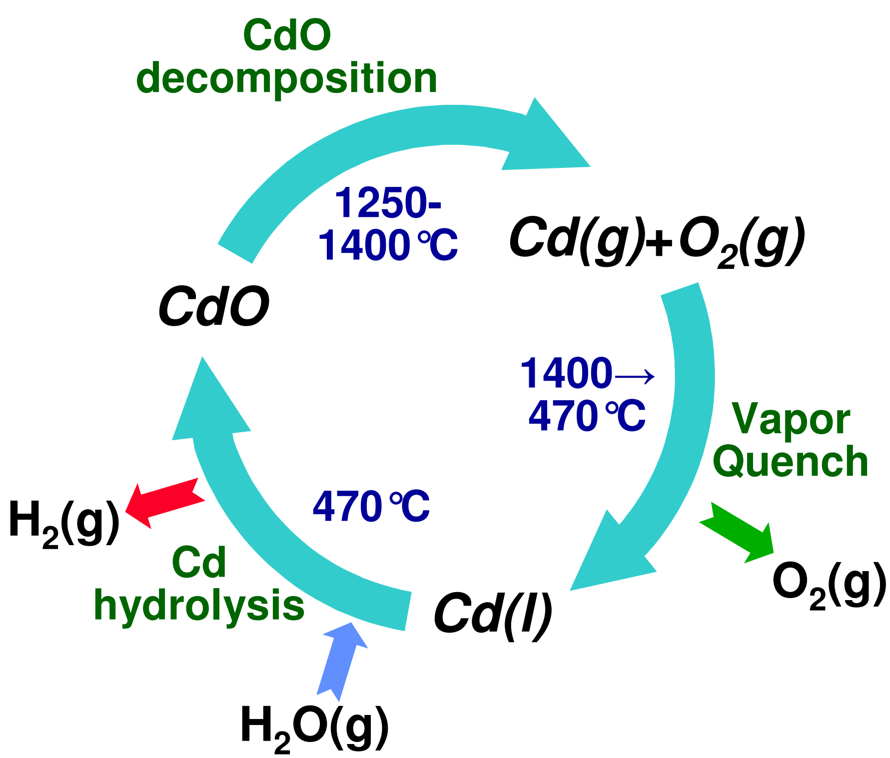
Cadmium Oxide Cycle Status



- A two step thermochemical cycle with a calculated efficiency of 59%(LHV)
- Feasibility of decomposition and hydrolysis steps have been demonstrated
- Diurnal process flowsheet using Aspen Plus has been completed
- Conceptual decomposer design incorporating vapor quenching has been established
- Preliminary H2A studies resulted in \$4.50 /kg H_2 for 2015
- Need to optimize solar field design and determine detailed recombination kinetics
- Prototype rotary kiln for Cadmium hydrolysis is being tested

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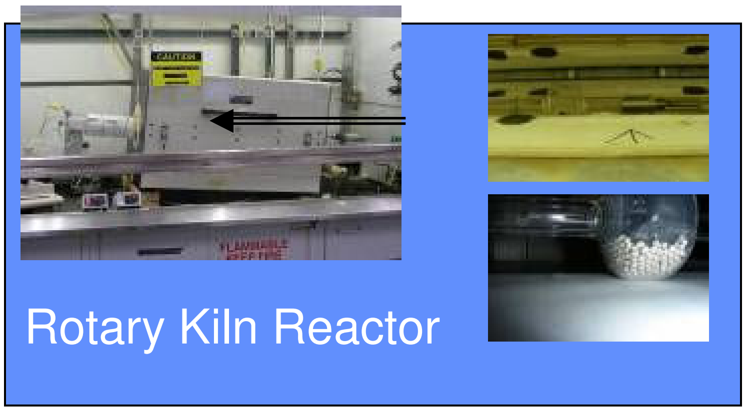
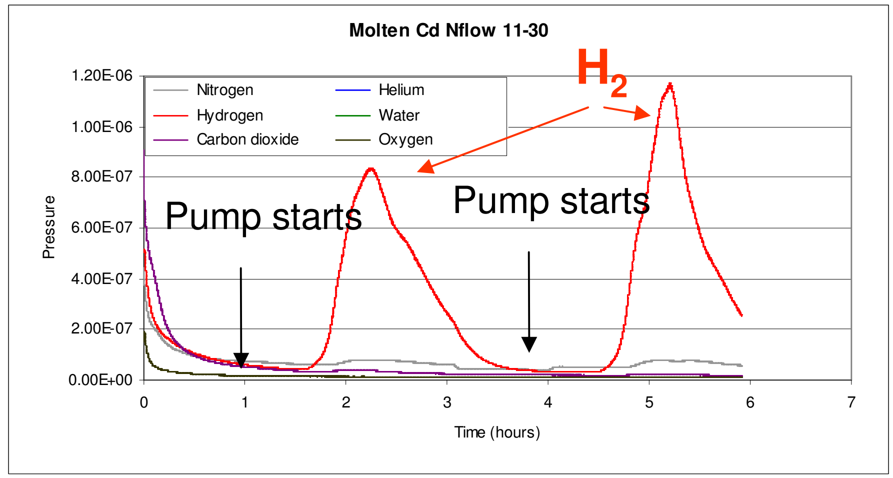
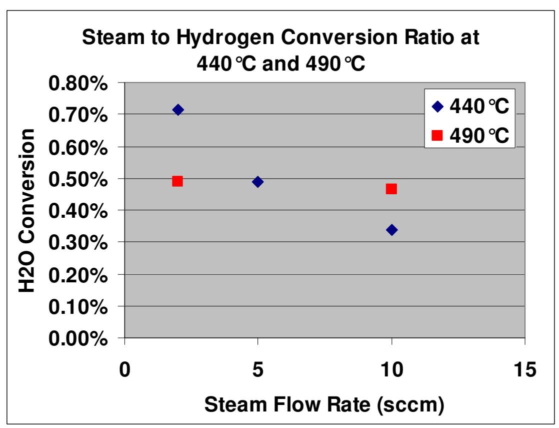
Hydrogen Production via Cadmium Hydrolysis

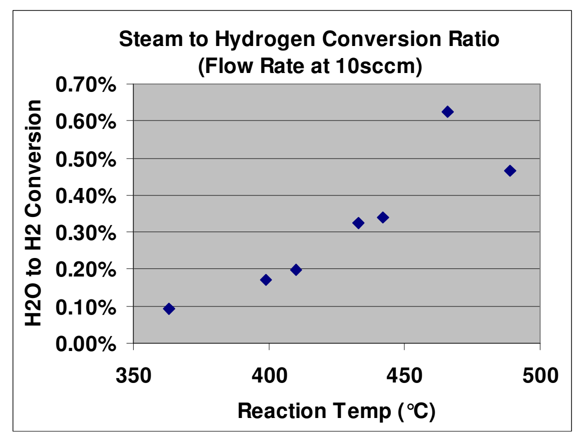
The steam to hydrogen ratio was evaluated for Cd hydrolysis



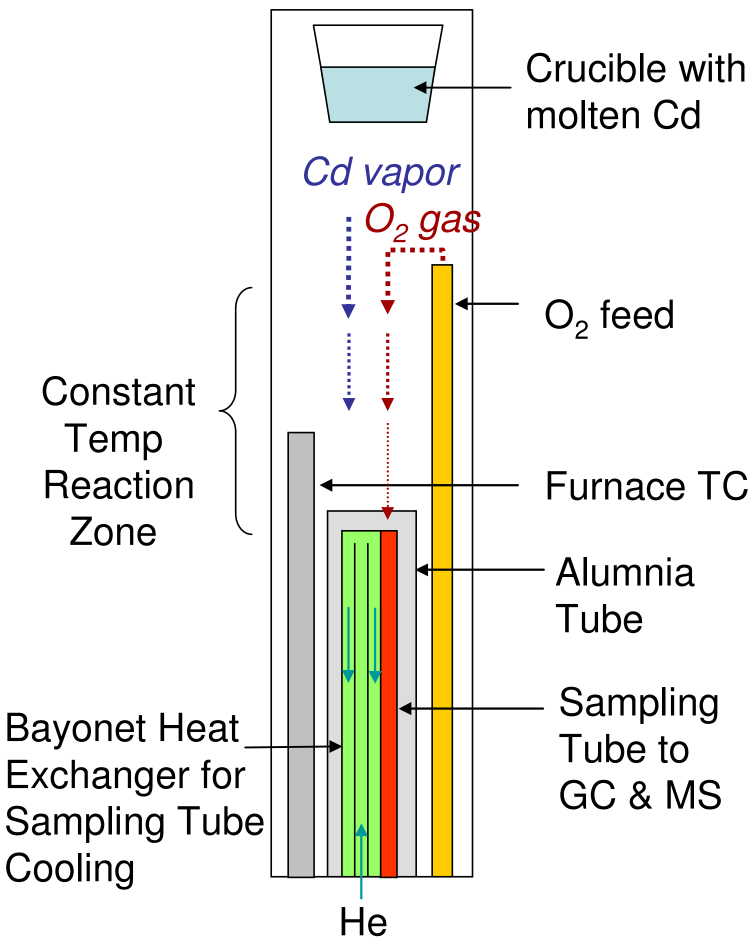


The largest conversion is at the Cd melting point ~470 C





Evaluation of Cd – O_2 Back Reaction



Modified TGA Set Up for Reaction Rate Measurements

The back reaction rate between Cd and O_2 was evaluated.

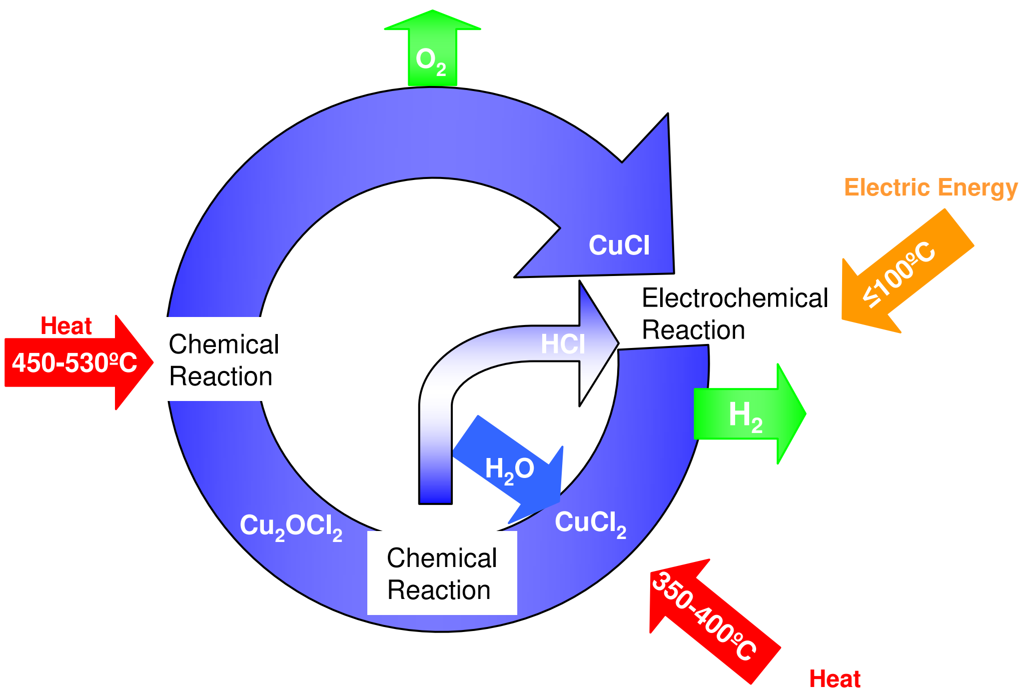
This information supports to design of a quench system to maximize Cd (and H_2) yields

Cadmium recombination rate

Temp (°C)	5*	2	1
1033	35.5**	44.5	47.4
1476		31.5	

** cadmium-oxygen reaction rate (%/s)
*O_2 flow rate (ml/min) total 150ml/min

Cu-Cl cycle & its advantages



The Hybrid Cu-Cl Cycle

- Lab-scale proof-of-concept experiments completed
  - **No show stoppers**
  - **550 C maximum temperature**
  - **Suitable with power tower solar technology**
  - **High yields without catalysts for thermal reactions**
- International support
  - **Atomic Energy of Canada developing the electrolyzer**
- 7 universities in US and Canada involved in R&D effort
  - **Membrane development, measurement of thermodynamic properties of $CuCl_2$-CuCl-HCl solutions, electrochemistry, risk analysis, etc.**

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Process Development Status

- Conceptual process design completed
  - **Aspen simulation used for mass and energy balance**
    - **Efficiency calculated as 40% (LHV)**
  - **Capital and operating costs estimated**
  - **Further refinement ongoing**

- H2A analysis based on Solar Two Plant (Sandia) and conceptual process design
  - **\$4.38 /kg H_2 for 2015 and \$3.01/kg H_2 for 2025**

- Initiated engineering lab-scale work
  - **Test key steps in the conceptual design**
  - **First set of results very promising**

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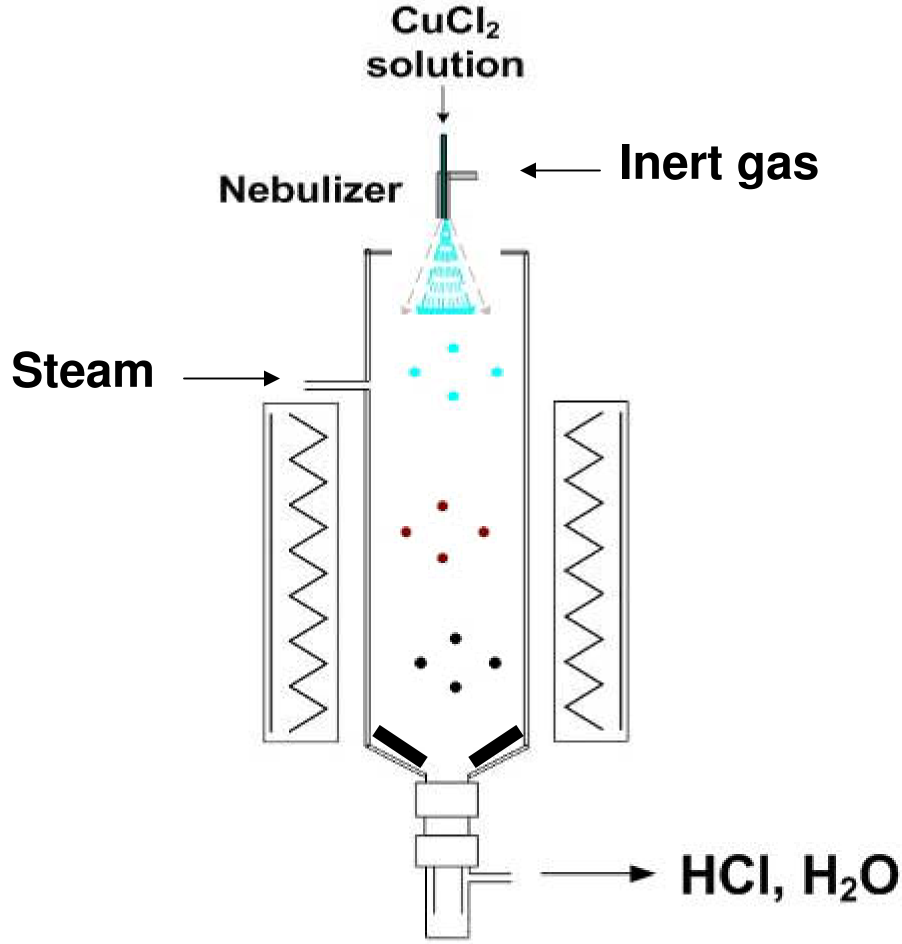
Key hydrolysis reaction demonstrated: $CuCl_2 + H_2O = Cu_2OCl_2 + HCl$

- Nebulizer reactor design concept successful
  - High heat and mass transfer zone
  - Very fine black powders of Cu_2OCl_2 produced

Nebulizer Furnace

Reaction Vessel



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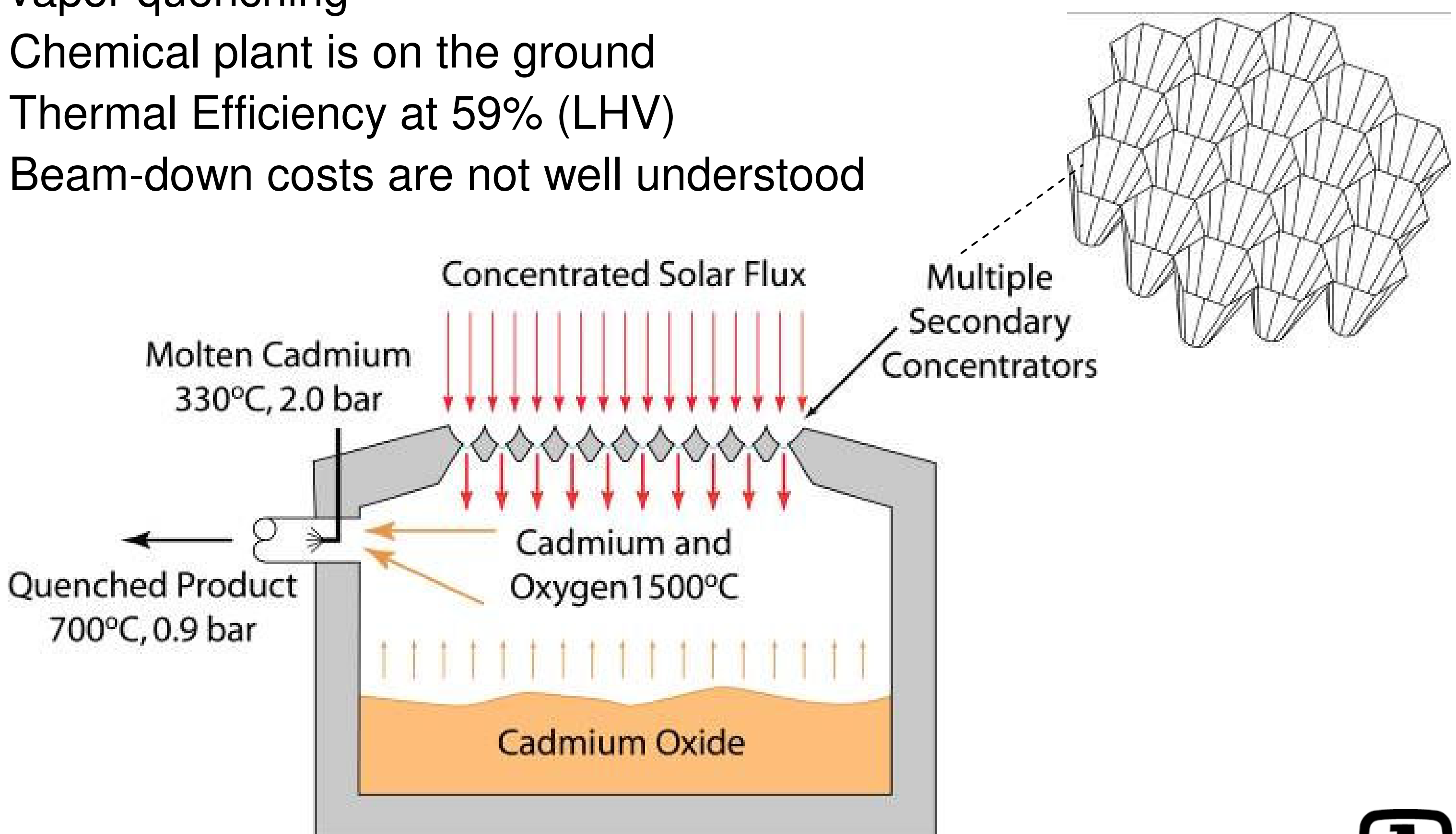
Solar Interface Development

Innovative Decomposer Design for a Beam Down Solar Tower

- Incorporates cadmium oxide decomposition and cadmium vapor quenching
- Chemical plant is on the ground
- Thermal Efficiency at 59% (LHV)
- Beam-down costs are not well understood



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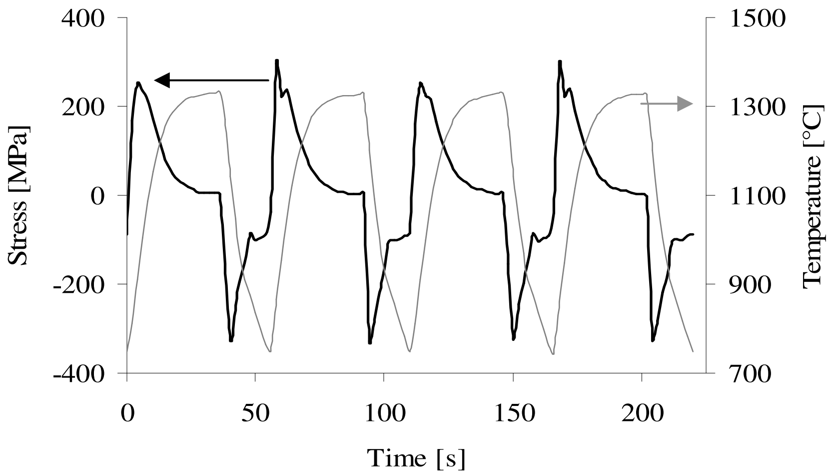
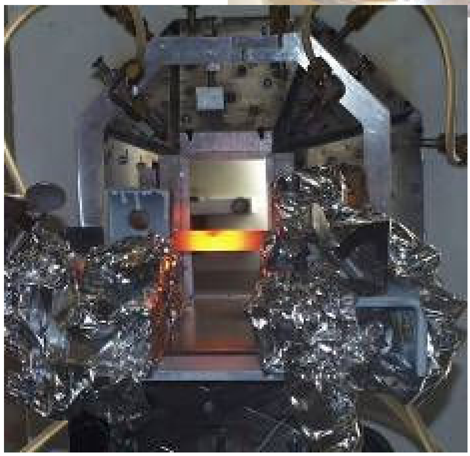
Multi-Tube Aerosol Reactor for Mn and Zn Cycles

- Tube array designed to intercept reflected and re-emitted radiation
- Tube material: Al_2O_3, SiC, and Haynes 214
- Design anticipated to yield improved efficiency for moderate to high temperatures (>1200 °C)


Prototype Reactor



Thermal Stress Plots


Tube Material Under Test

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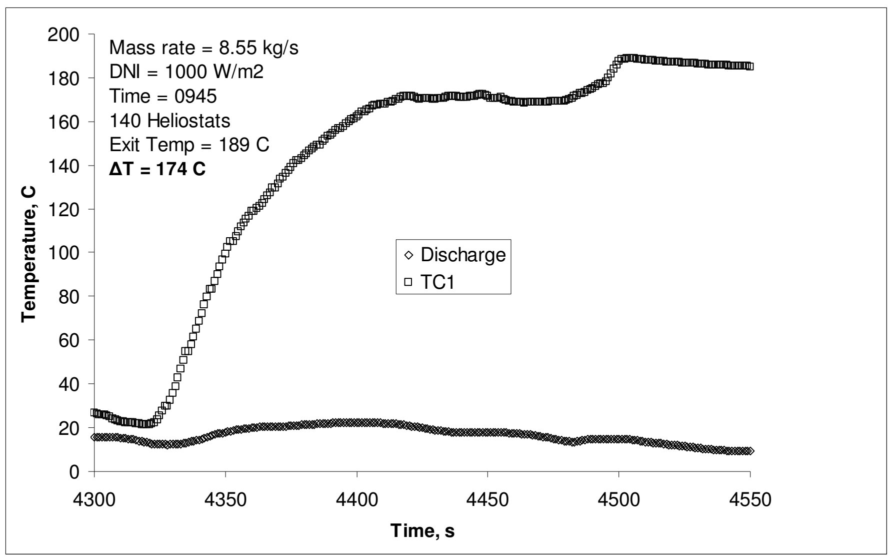
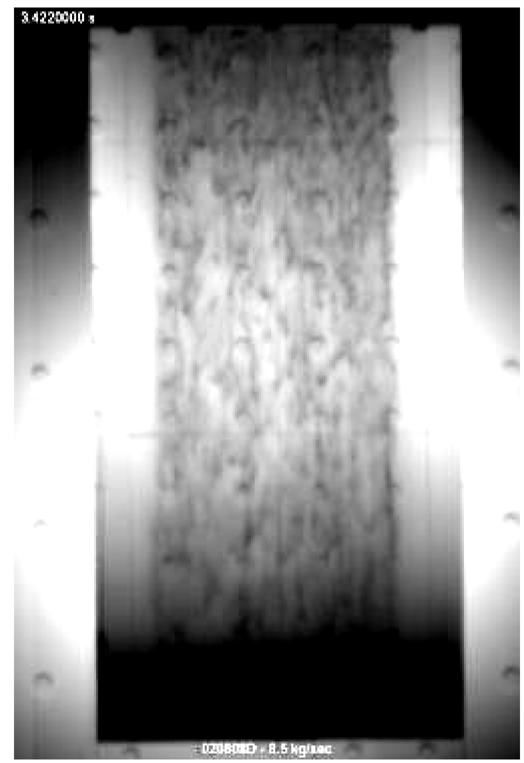
Solid Particle Receiver On-Sun Testing

- SPR evaluated on-sun at 2.5 MW_{th} level
- Demonstrated Single pass ΔT of ~200 C
- Target ΔT (SI-HyS) is between 300 – 500 C
- Materials evaluation underway

SPR on the Power Tower



Typical Particle Heating Results

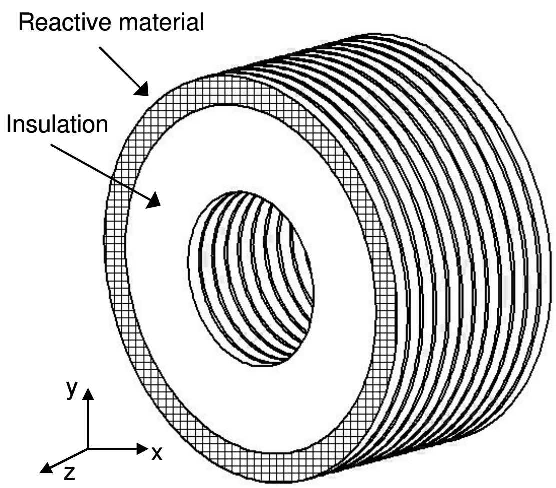


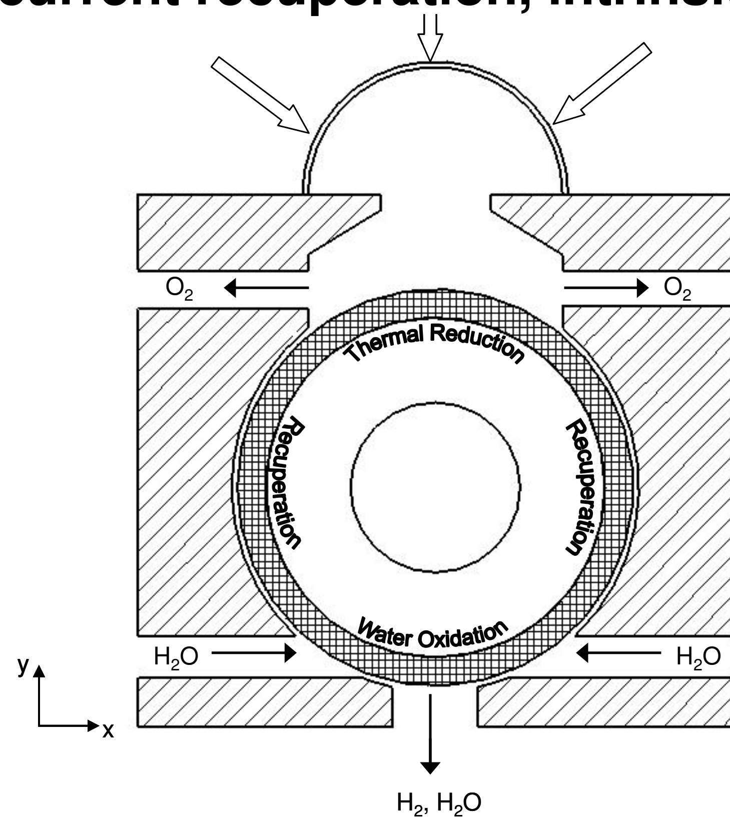
Particle Curtain On-Sun

Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

- Thermochemical heat engine concept
  - Converts thermal energy to chemical work
  - Analogous to mechanical heat engines
- Incorporates transport of ferrite, thermal reduction and hydrolysis reactors, countercurrent recuperation, intrinsic separation of H_2 and O_2

Set of Counter-Rotating Rings





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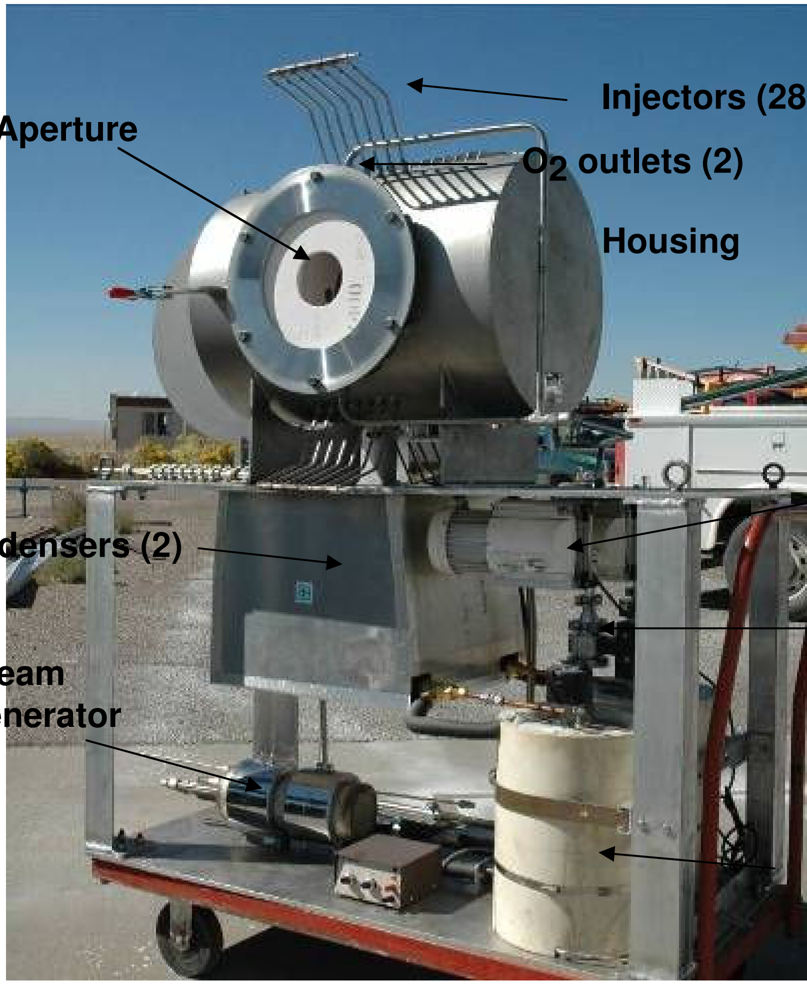
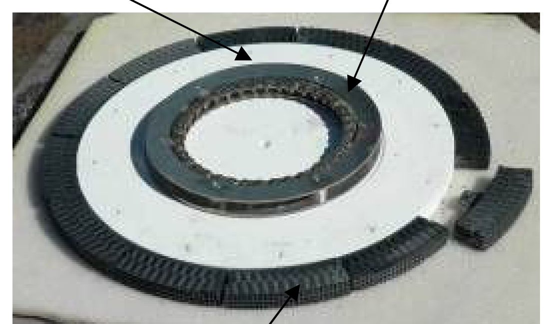
CR5 Prototype Construction



- Reactor and auxiliary equipment ready
- Reactant fins in production
  - 12 segments per ring
  - Glued and pinned in place
  - 14 rings in prototype



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H2A Economics

H2A Analyses – Current Status

We have worked with the different teams to help ensure that the hydrogen production ($/kg) cost analyses have common and reasonable assumptions, enabling effective decision making.

Goal: Complete H2As for *ALL* cycles before the end of FY2008 to inform cycle down select.

Current Status:

- ***Hybrid Sulfur* – Nearly complete for 2015 and 2025; will work with SRNL and SNL to modify cycle for solar (vs. nuclear)**
- ***Zn/ZnO* – Need to complete additional refinements for 2015 and 2025 cases**
- ***CuCl* – Working to refine electrolyzer costs**
- ***Ferrite* – Very preliminary design and H2A completed**
- ***Cd/CdO* – Need updated H2As with new solar field**
- ***Solar-Thermal Electrolysis* – Need vetted solar thermal electricity price from DOE Solar Office**
- ***S-I (Reactive)* – Preliminary H2A done, will refine together with SRNL, Technology Insights**
- ***Manganese Oxide, Ammonium Sulfate* – No H2A received to date.**

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Current H2A Cost Estimates

Comparison of current cost estimates:

	2015	2025	Comments
Cd / CdO	Under revision	Not available	Cycle under revision
CuCl	**$4.30**	**$2.82**	Electrolyzer cost highly uncertain
Ferrite	**$5.52**	Not available	Very preliminary
Hybrid Sulfur	**$4.37**	**$2.91**	Solar electric cost important
Zn / ZnO	**$5.07**	**$3.62**	Solar field + receiver cost, performance questions
S-I	**$3.86 - $4.60**		Very preliminary

The cost estimates are central to the upcoming cycle down selects coming in 2008. Specifically, if a cycle does not have a plausible path to attaining DOE hydrogen cost goals in 2025, DOE-funded work on the cycle is unlikely to continue.

Future Work

- Continually update H2A analyses on all prospective cycles
- Continue feasibility and system design efforts
- Demonstrate solar interfaces on-sun
- Downselect to 1-2 best cycles at the end of FY08
- Develop an R&D plan to carry forward the 1-2 best cycles to a pilot scale demonstration
- *FY09 DOE/EERE budget request for hydrogen production is $0*

Summary

- ***Objective***
  - Identify 1-2 solar thermochemical routes to cost effective hydrogen production
- ***Approach***
  - Evaluate the feasibility of associated chemical reactions and develop appropriate solar interfaces. Support this work with an economic evaluation.
- ***Technical Accomplishments***
  - Feasibilty studies are progressing, solid particle receiver has been demonstrated, other receiver concepts nearing demonstration, H2A analysis is underway
- ***Future Work***
  - Continue feasibility studies – expanding ferrite efforts, update H2A on all cycles, downselect to 1-2 best cycles, develop future R&D plan to support pilot-scale demo

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Response to Reviewer's Comments

- *Downselect to 1-2 cycles*
  - This is planned for the end of FY08
- *Focus on materials development*
  - We are currently investigating materials development to support the solid particle receiver, the ferrite cycles, and the Mn/Zn cycles.
- *Heliostat cost reduction*
  - Heliostat costs must decrease from $180/m2 to $80/m2 in 2017
  - The research effort needed to support cost reductions is outlined in:
    - Heliostat Cost Reduction Study - SAND2007-3293

Critical Assumptions and Issues

- ***Cost***
  - H2A is an accepted methodology used to assess each system based on common assumptions.
- ***Parasitic system losses***
  - Process flowsheeting can be used as a starting point. Information from the feasibility studies is a required input.
- ***High temperature materials operation***
  - Extreme environments degrade materials thermally and chemically. On-sun and lab scale testing are key to addressing this issue.

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Publications

- Richard B. Diver, Nathan P. Siegel, James E. Miller, Timothy A. Moss, John N. Stuecker, Darryl L. James, 2008, “Development of a CR5 Solar Thermochemical Heat Engine Prototype,” Proceedings of 2008 14th Biennial CSP Solar PACES Symposium, Las Vegas, NV.
- James E Miller, Ph.D; Mark D Allendorf, Ph.D.; Richard B Diver, Ph.D.; Lindsey R Evans, Nathan P Siegel, Ph.D.; John N Stuecker, 2008, Metal Oxide Composites and Structures for Ultra-High Temperature Solar Thermochemical Cycles, Journal of Material Science, In Press.
- Kolb, G.J., Jones, S.A., Donnelly, M.W., Gorman, D., Thomas, R., Davenport, R., Lumia, R., “Heliostat Cost Reduction Study”, Sandia Internal Report, SAND2007-3293.
- Huajun Chen, Yitung Chen, Hsuan-Tsung Hsieh, and Nate Siegel, 2007, “CFD Modeling of Gas Particle Flow within a Solid Particle Solar Receiver,” *Journal of Solar Energy Engineering*, Vol. 129, pp. 160-170, May 2007.
- Huajun Chen, Yitung Chen, and Hsuan-Tsung Hsieh, “Numerical Investigation on Optimal Design of Solid Particle Solar Receiver,” Proceedings of the ASME Energy Sustainability, ES2007-36134, June 27 - 30, Long Beach, CA, 2007.

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