# 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**

**Project ID # PD13**

# 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

# 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** | $\$/\text{kg H}_2$ | *10.00* | **6.00** | **3.00** |
| **Heliostat Capital Cost** | $\$/\text{m}^2$ | *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

# 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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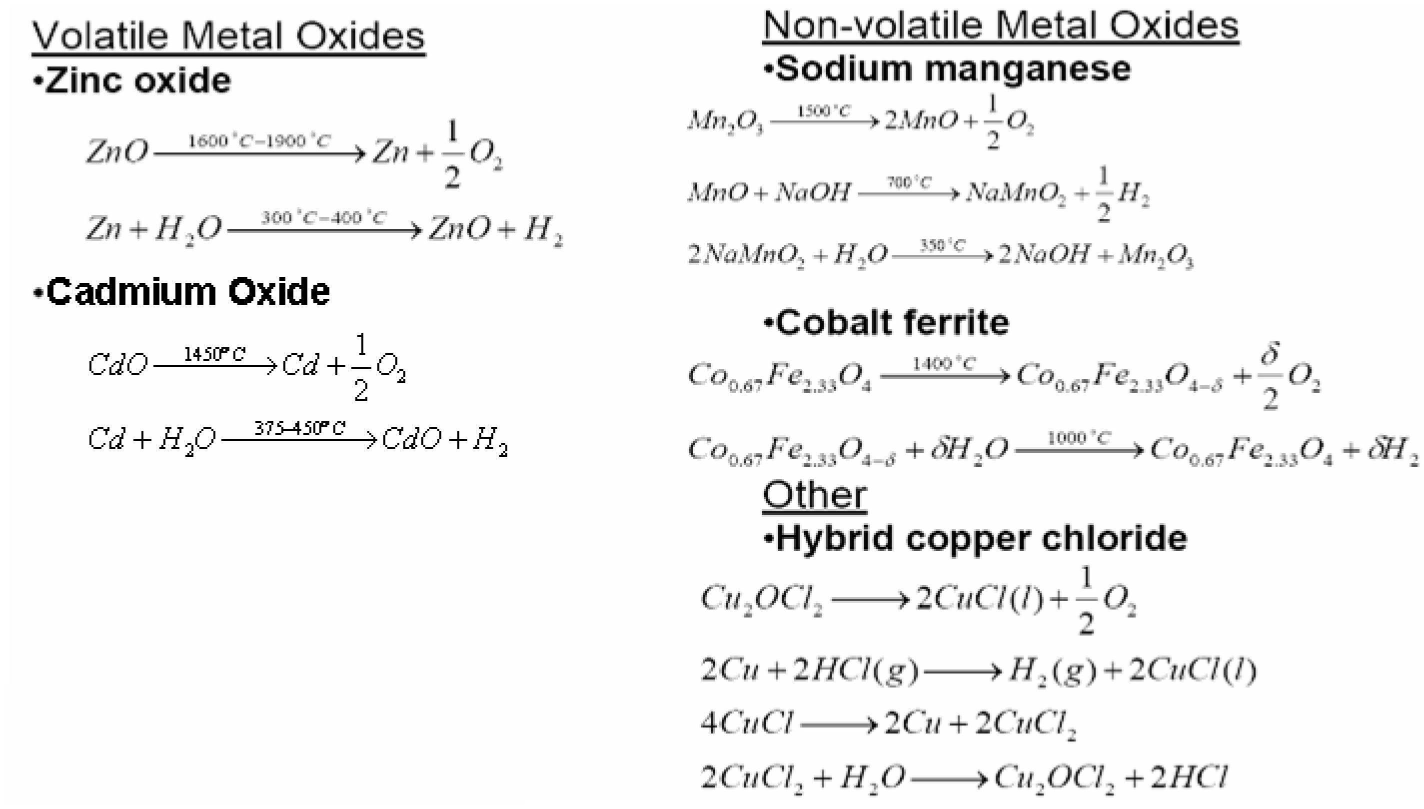
# Cycle Feasibility Studies

# 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**

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

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

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

**•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**

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

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

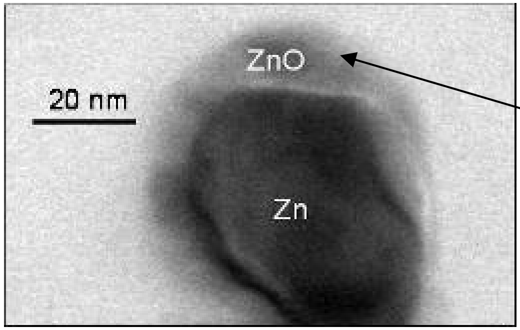
$$4CuCl \longrightarrow 2Cu + 2CuCl_2$$

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

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

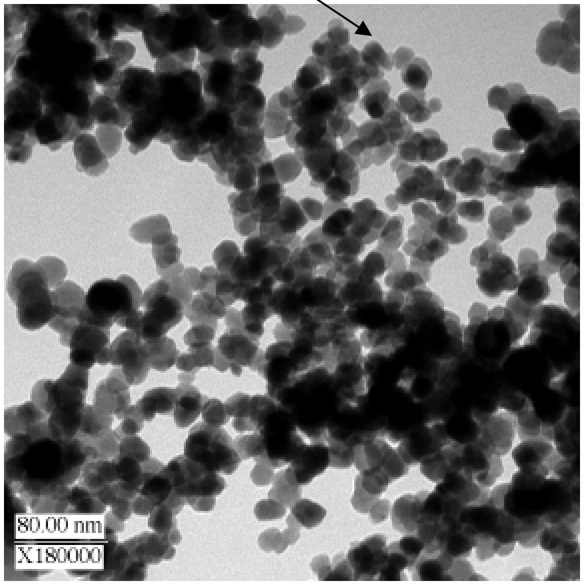
# Progress in the Zn/ZnO Cycle

- **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**

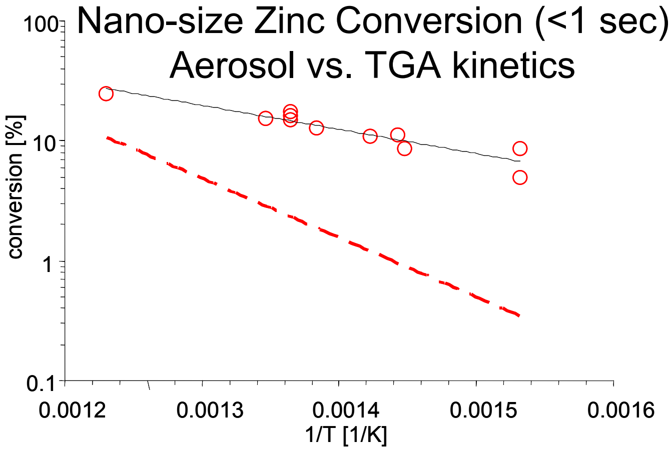


*Passivating ZnO film*

- **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**

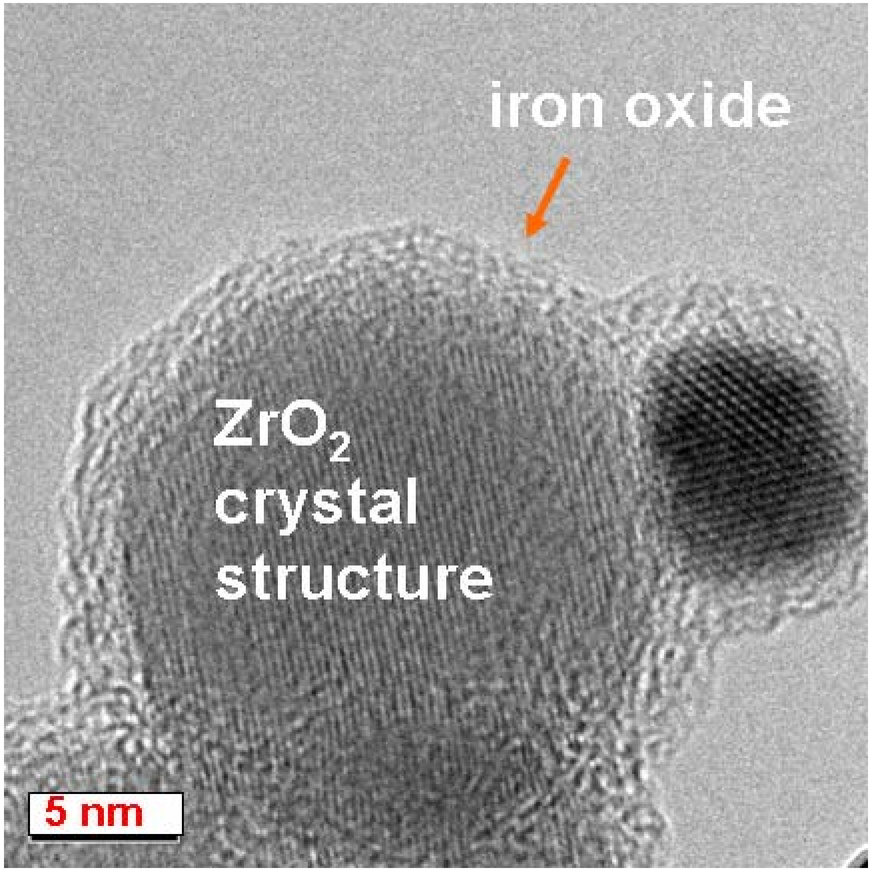


Aerosol processing can give fast rates for many high temperature cycles

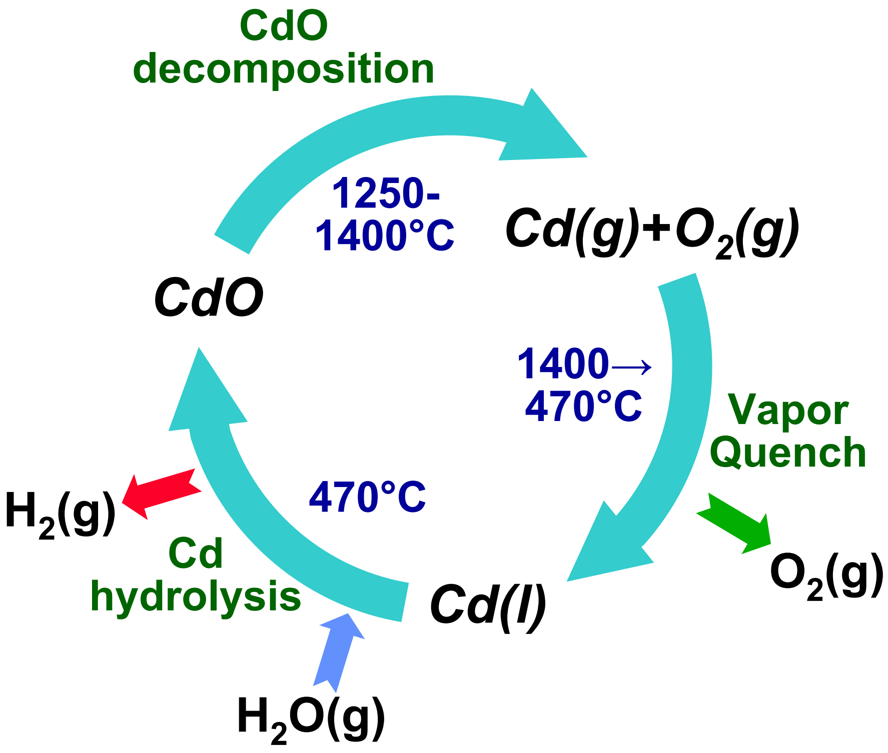


# Atomic Layer Deposition (ALD) of $Co_xFe_{3-x}O_4$

- *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



# 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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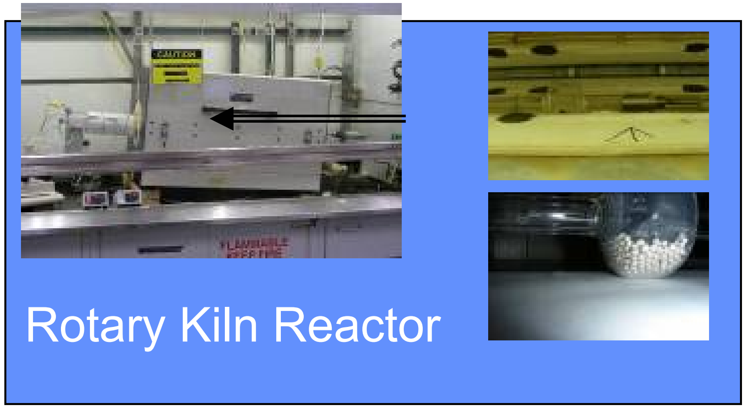
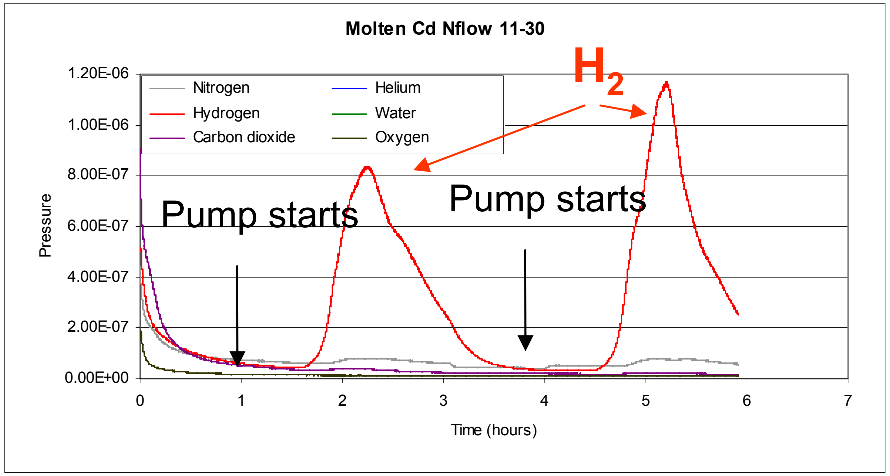
# Hydrogen Production via Cadmium Hydrolysis

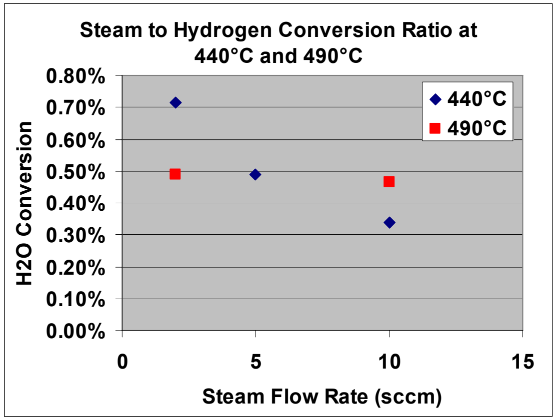
***The steam to hydrogen ratio was evaluated for Cd hydrolysis***

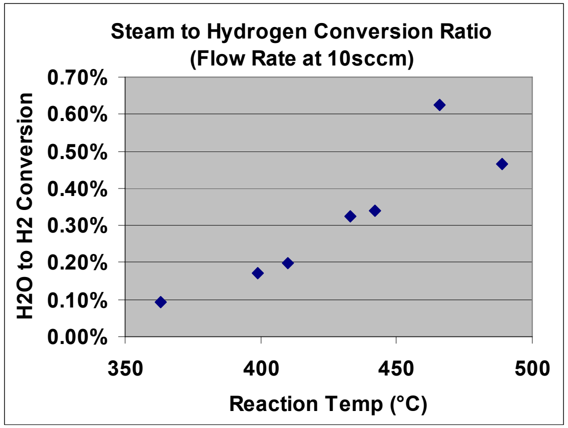


Rotary Kiln Reactor

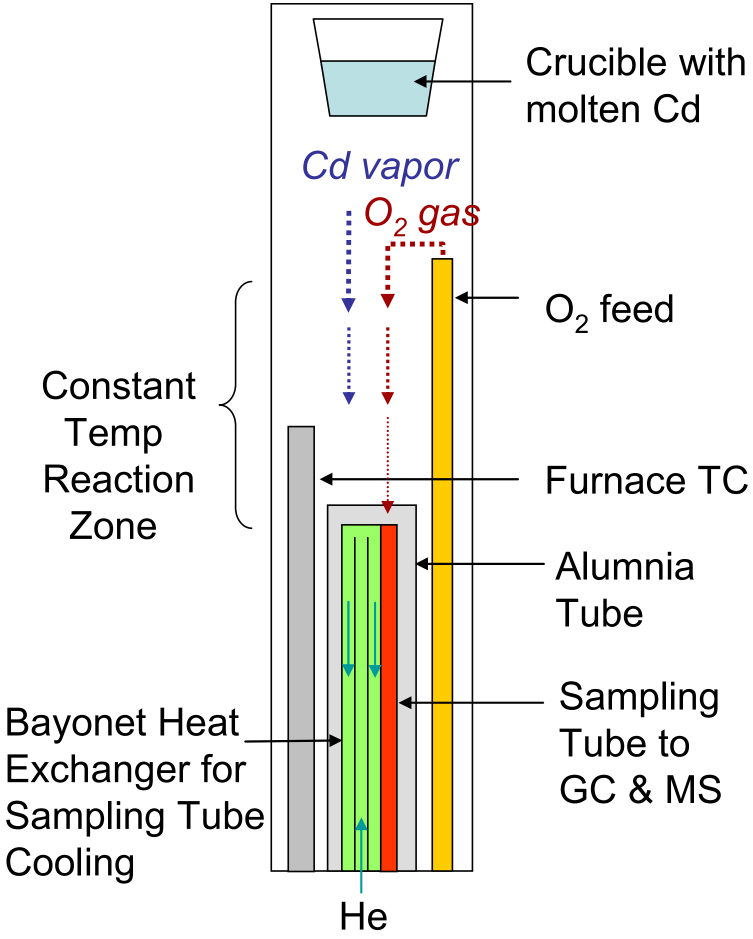


***The largest conversion is at the Cd melting point ~470 C***





# 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.***

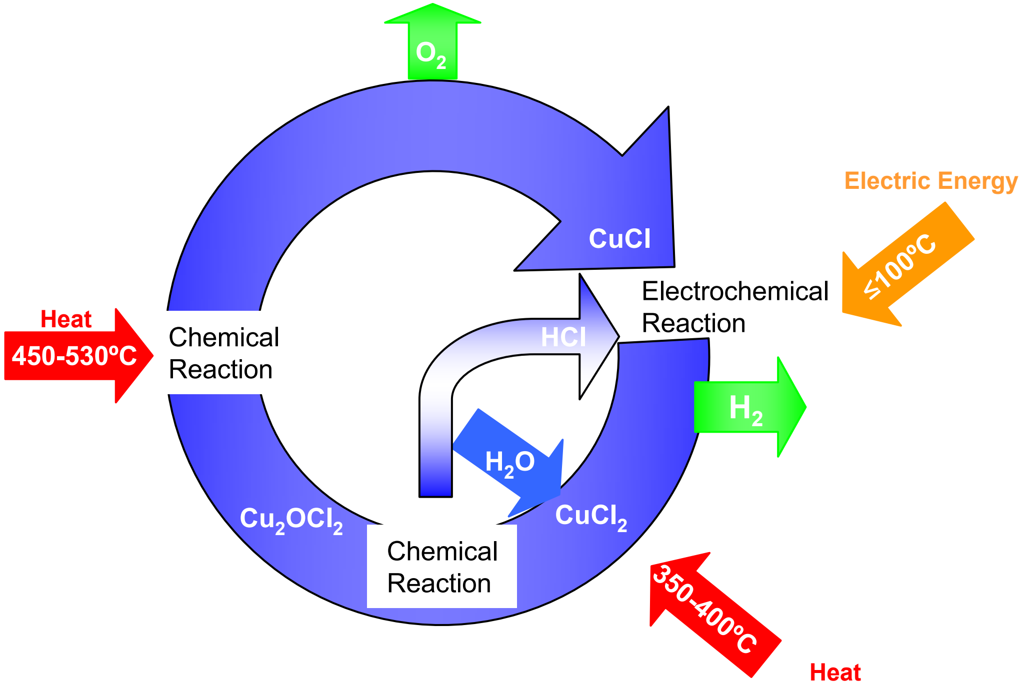
***This information supports to design of a quench system to maximize Cd (and $H_2$) yields***

**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.**

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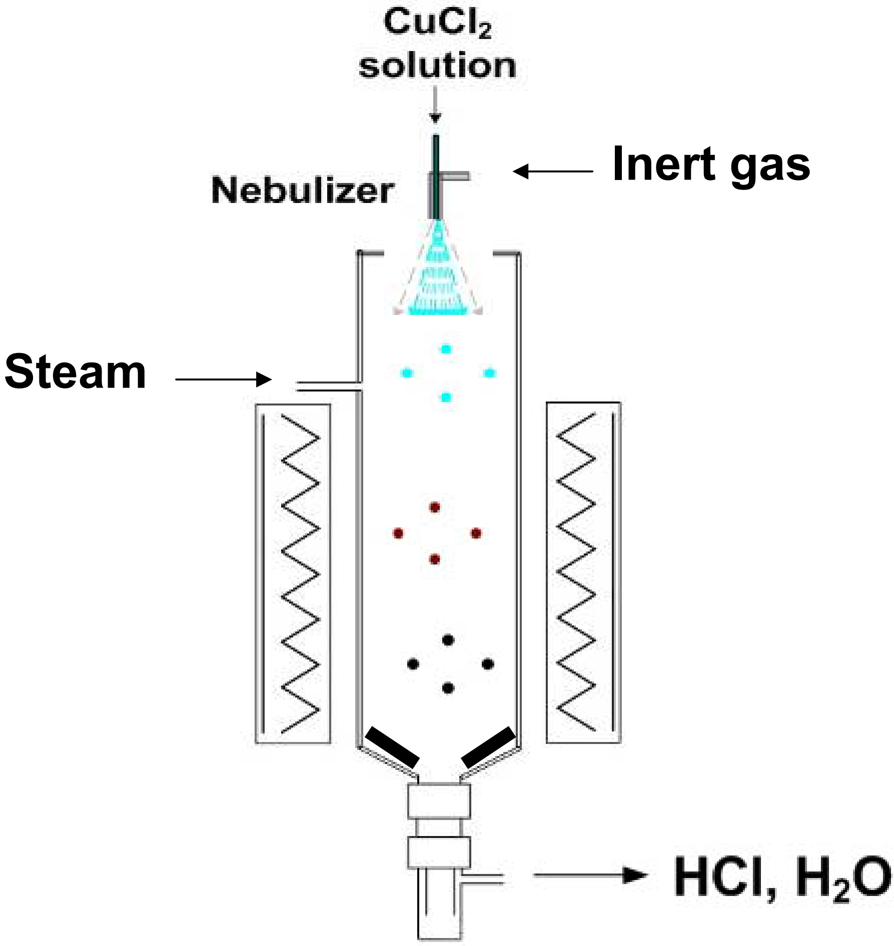
# Key hydrolysis reaction demonstrated: $CuCl_2 + H_2O = Cu_2OCl_2 + HCl$

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



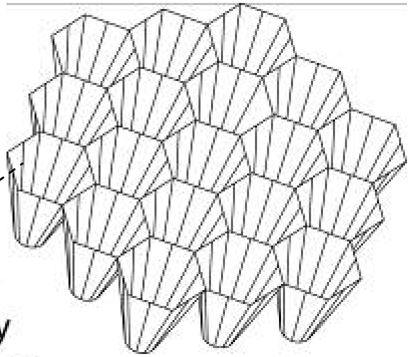
*Nebulizer Furnace*

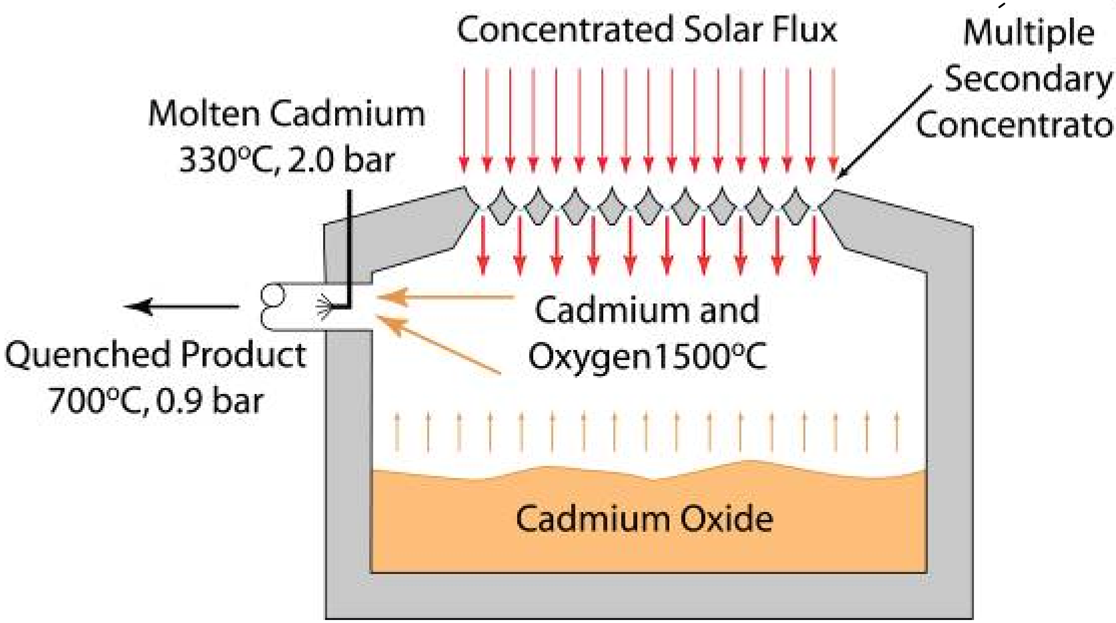
*Reaction Vessel*

# 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

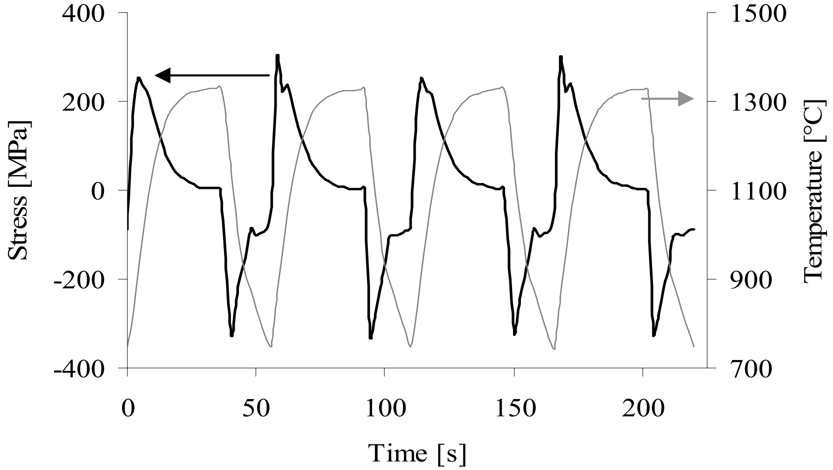




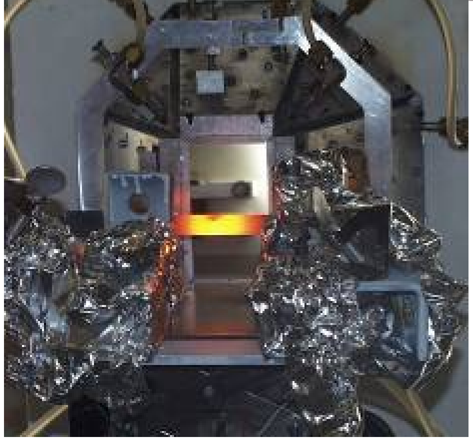
# Multi-Tube Aerosol Reactor for Mn and Zn Cycles

- **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*

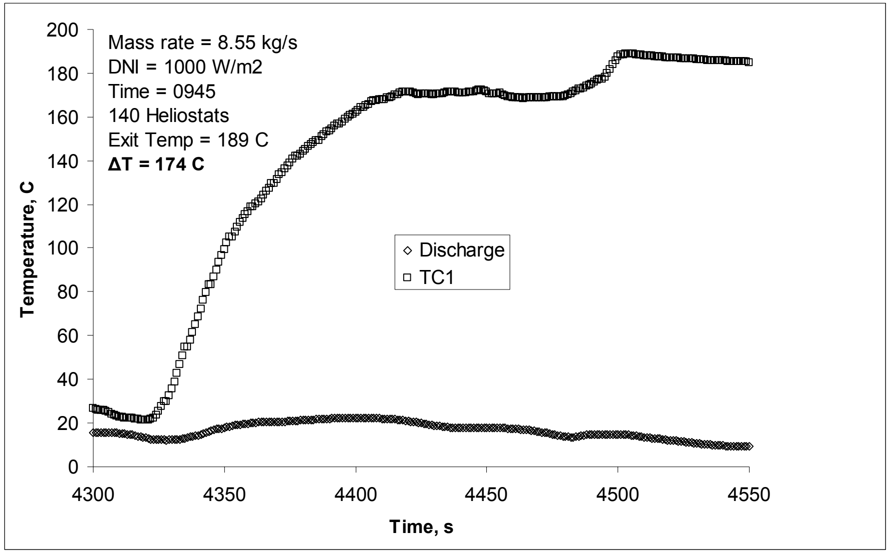


*Tube Material Under Test*

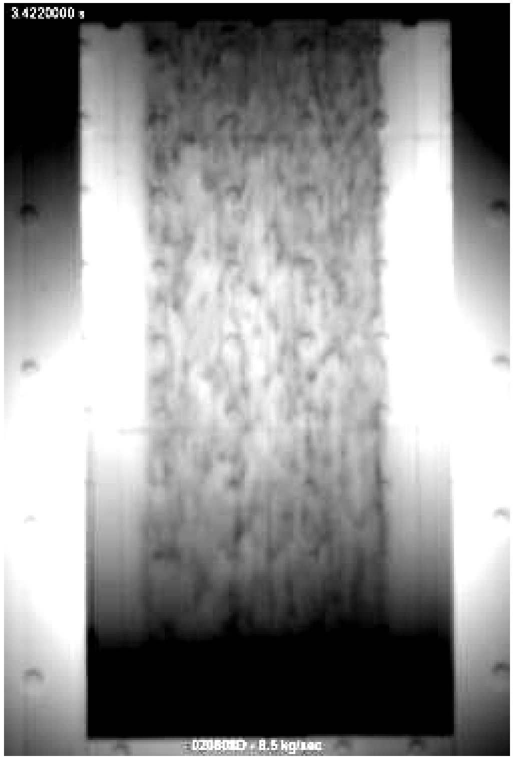
# Solid Particle Receiver On-Sun Testing

- 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*



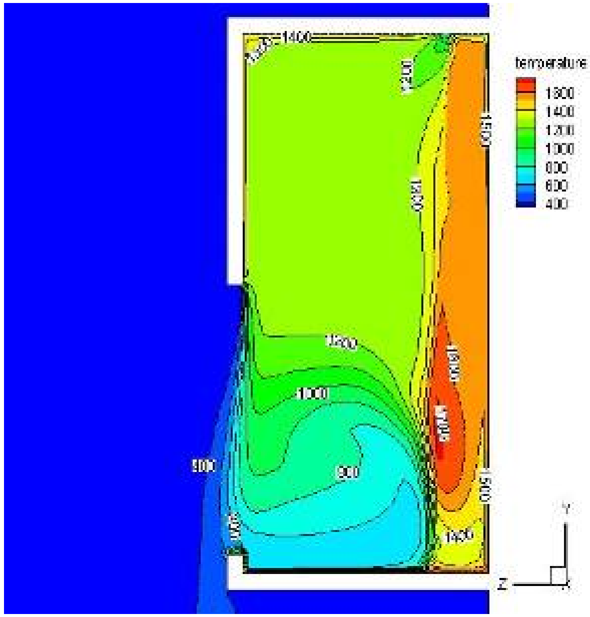
*Typical Particle Heating Results*



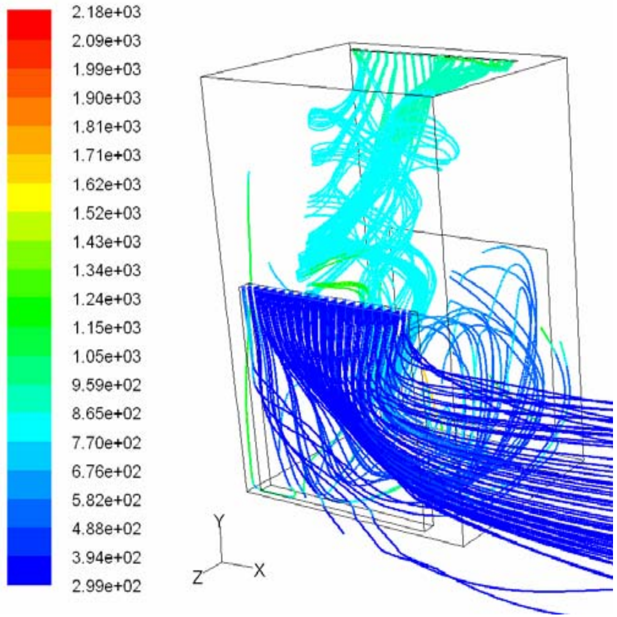
*Particle Curtain On-Sun*

# Numerical Models Support SPR Design

- Computational models are developed to assess receiver performance and efficiency
- Data from on-sun testing is being used to validate the complex models
- Validated models will be used in future SPR designs



*Internal Cavity Air Temperature*



*Pathlines showing internal currents*

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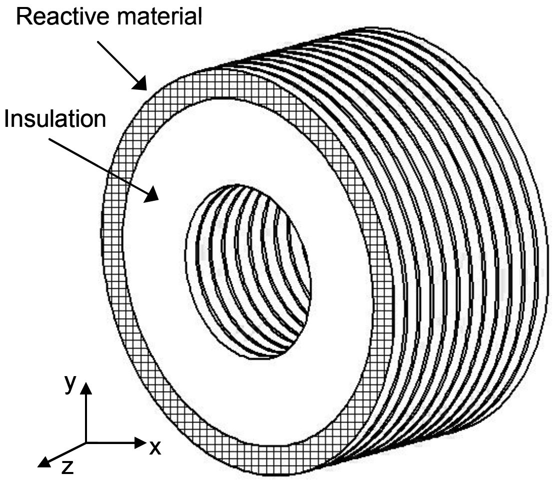
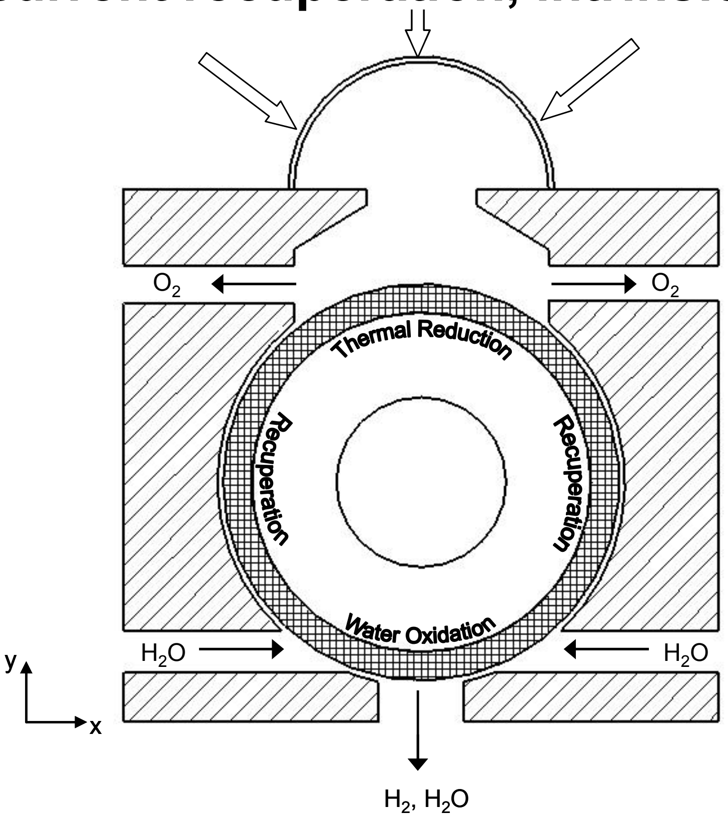
# Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

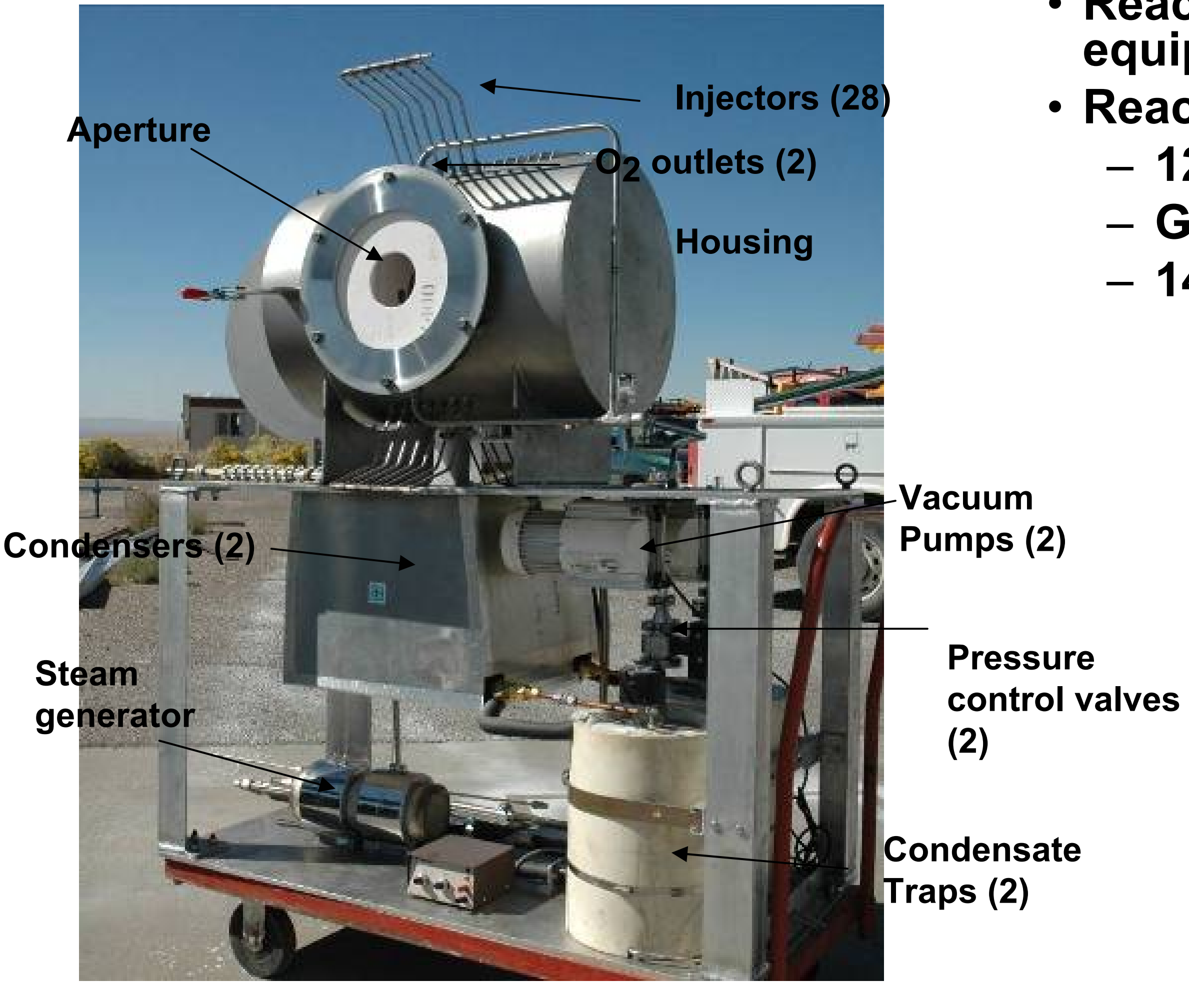
- Thermochemical heat engine concept
  - Converts thermal energy to chemical work
  - Analogous to mechanical heat engines
- Incorporates transport of ferrite, thermal reduction and hydrolysis reactors, countercurrent recuperation, intrinsic separation of $H_2$ and $O_2$

Set of Counter-Rotating Rings

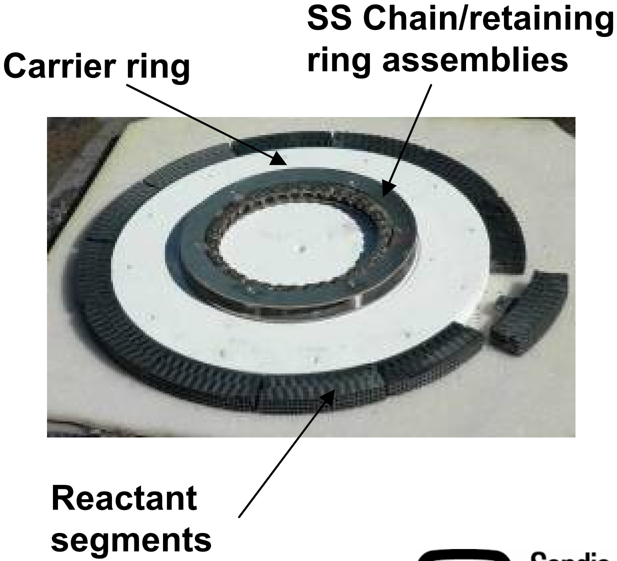




# CR5 Prototype Construction



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



# 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 cyles, downselect to 1-2 best cycles, develop future R&D plan to support pilot-scale demo