Development of Solar-powered Thermochemical Production of Hydrogen from Water

Al Weimer for the Solar Thermochemical Hydrogen (STCH) Team

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UNLV Research Foundation
Las Vegas, Nevada

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

Project ID No. PD10

Overview

Timeline

- 6-25-2003
- 12-31-2005
- 40%

Budget

- Total Project Funding
  - $5,614,049 DOE
  - $752,900 Cost share
- Funds received in FY04
  - $2,943,232

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 The University of Hawaii Sandia National Laboratories The National Renewable Energy Laboratory Argonne National Laboratory General Atomics Arizona Public Service General Electric General Motors ETH-Zurich MVSystems, Inc. Intematix, Inc.

Objectives

- Identify a cost competitive solar-powered water splitting process for hydrogen production
- Continue experimental cycle studies needed for final quantitative selection
- Numerical and experimental evaluation of solid particle receiver performance
- Optimize heliostat/tower/secondary concentrator characteristics and configurations for various operating temperatures

Approach

- Design and implement a quantitative comparative assessment methodology to screen all known thermochemical cycles and select the top several performers
- Perform literature surveys and laboratory experiments to acquire essential evaluation and design data for the top several concepts
- Develop validated designs for collector system components for integrated system analysis
- Analyze cost and efficiency metrics for integrated cycle performance
- Develop demonstration plant concept design(s) for surviving competitive cycle(s) and provide recommended path forward

Technical Accomplishments/ Progress/Results

- Cycle database and scoring are completed
- Experimental work (kinetics, thermodynamics, and product characterization) underway for five cycles
- Some system designs optimized for various operating temperatures and power requirements
- CFD modeling and simulation carried out to develop understanding of thermal transport in reactors and solid particle receivers

Discovery and assessment of known thermochemical cycles is completed

- 353 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**
- Hybrid Cadmium
- **Cadmium Carbonate**

Non-volatile Metal Oxides

- Iron oxide
- **Sodium manganese**
- Nickel manganese ferrite
- Zinc manganese ferrite
- **Cobalt ferrite**

Other

- **Hybrid copper chloride**

~~Metal Sulfates~~

- ~~Cadmium sulfate~~
- ~~Barium-Molybdenum sulfate~~
- ~~Manganese sulfate~~

Sulfuric Acid (NHI)

- Hybrid sulfur
- Sulfur iodine
- Multivalent sulfur

Metal Sulfate Cycles were Eliminated from Consideration

"Sulfate cycles": $MO + SO_2 + H_2O = MSO_4 + H_2$
No experimental evidence reported.

Thermodynamically, this reaction is favorable, but side reactions are more favorable.

SHGR studied sulfate cycles with MO = MnO, BaO under a variety of conditions:

25-100°C, makes MSO_3 , **No H_2**

$MO + SO_2 = MSO_3$ for M = Mn, Ba

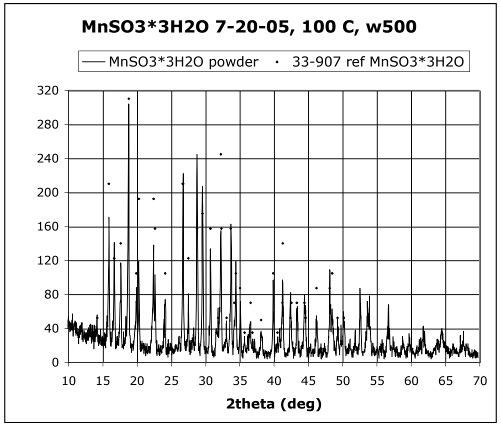
200-260°C, 100 atm, $MnSO_3$, **No H_2**

$MnO + SO_2 = MnSO_3$

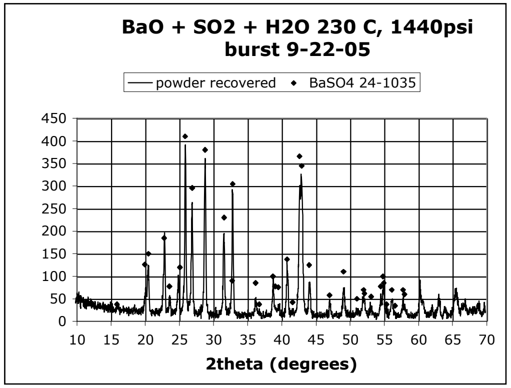
230-240°C, 100 atm, BaSO4 + S, **No H_2**

$2 BaO + 3 SO_2 = 2 BaSO_4 + S$

X-ray diffraction shows $MnSO_3$*$3H_2O$

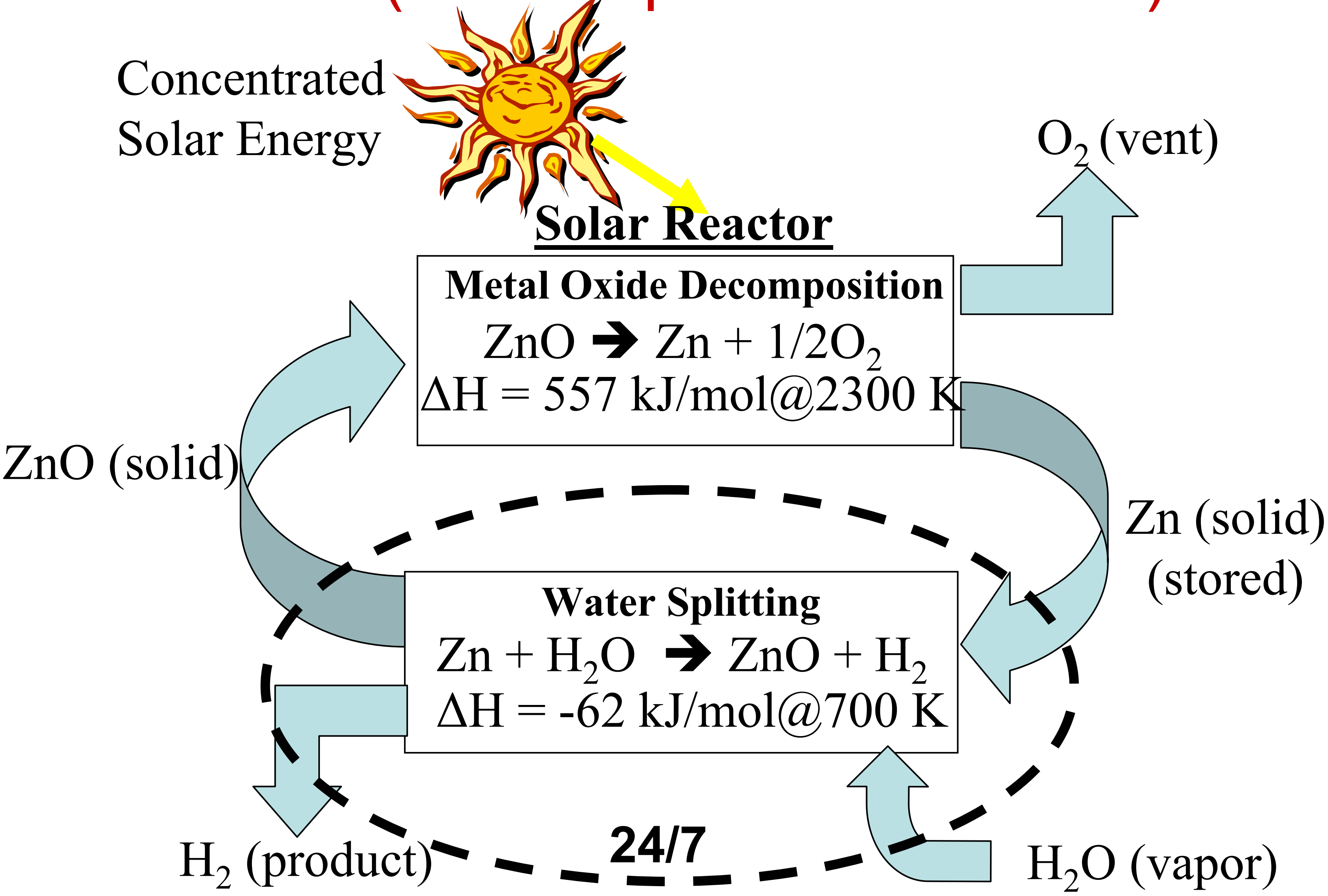


X-ray diffraction shows $BaSO_4$



We doubt that any "sulfate cycle" is feasible

Two step ZnO/Zn Process to split water
(both steps demonstrated)



Concentrated Solar Energy

Solar Reactor

Metal Oxide Decomposition

$ZnO \rightarrow Zn + 1/2O_2$

$\Delta H = 557$ kJ/mol@2300 K

O_2 (vent)

ZnO (solid)

Zn (solid) (stored)

Water Splitting

$Zn + H_2O \rightarrow ZnO + H_2$

$\Delta H = -62$ kJ/mol@700 K

H_2 (product)

24/7

H_2O (vapor)

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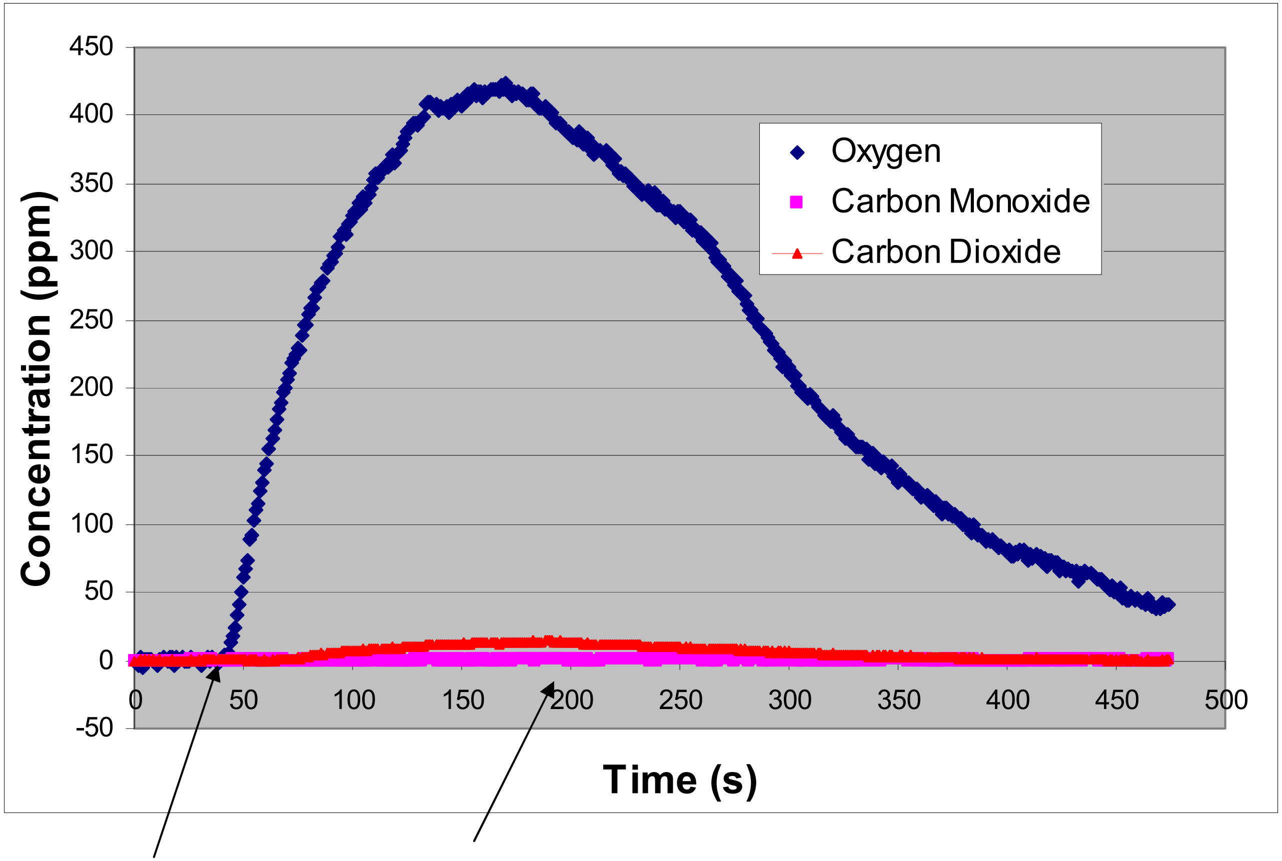
Aerosol ZnO Dissociation of ZnO

($ZnO \rightarrow Zn + 1/2O_2$; 1600 °C; Al_2O_3 tube)



Feeding initiated Feeding stopped

- Demonstration of rapid (< 1s) ZnO dissociation for Zn/ZnO cycle
- Highest conversion ever (>40%) for thermal dissociation of ZnO
- Conversion consistent with kinetic model

9 cm ID x 46 cm long Lab Transport Tube

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Kinetic Models for Zn/ZnO Cycle

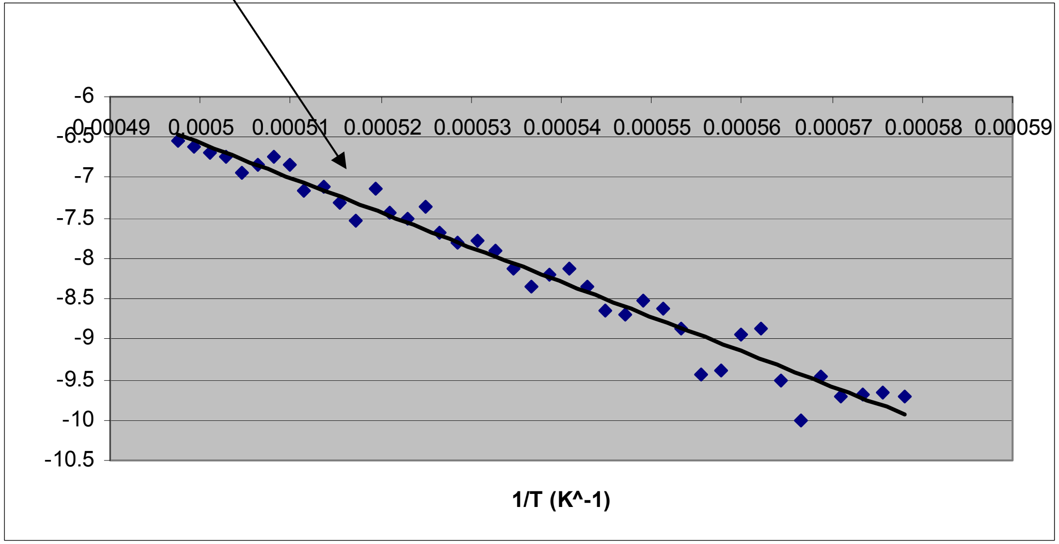
Thermogravimetric Analysis performed to determine kinetic expression

$$\frac{d\alpha}{dt} = k_0 e^{\left(\frac{-E_a}{RT}\right)} (1-\alpha)^{\frac{2}{3}}$$

$k0 = 9.30 \times 10^6 \pm 0.3 \times 10^6\ s^{-1}$

$E_a = 357.8 \pm 12\ kJ/mol$

Arrhenius analysis yielded excellent agreement with prevailing kinetic theory

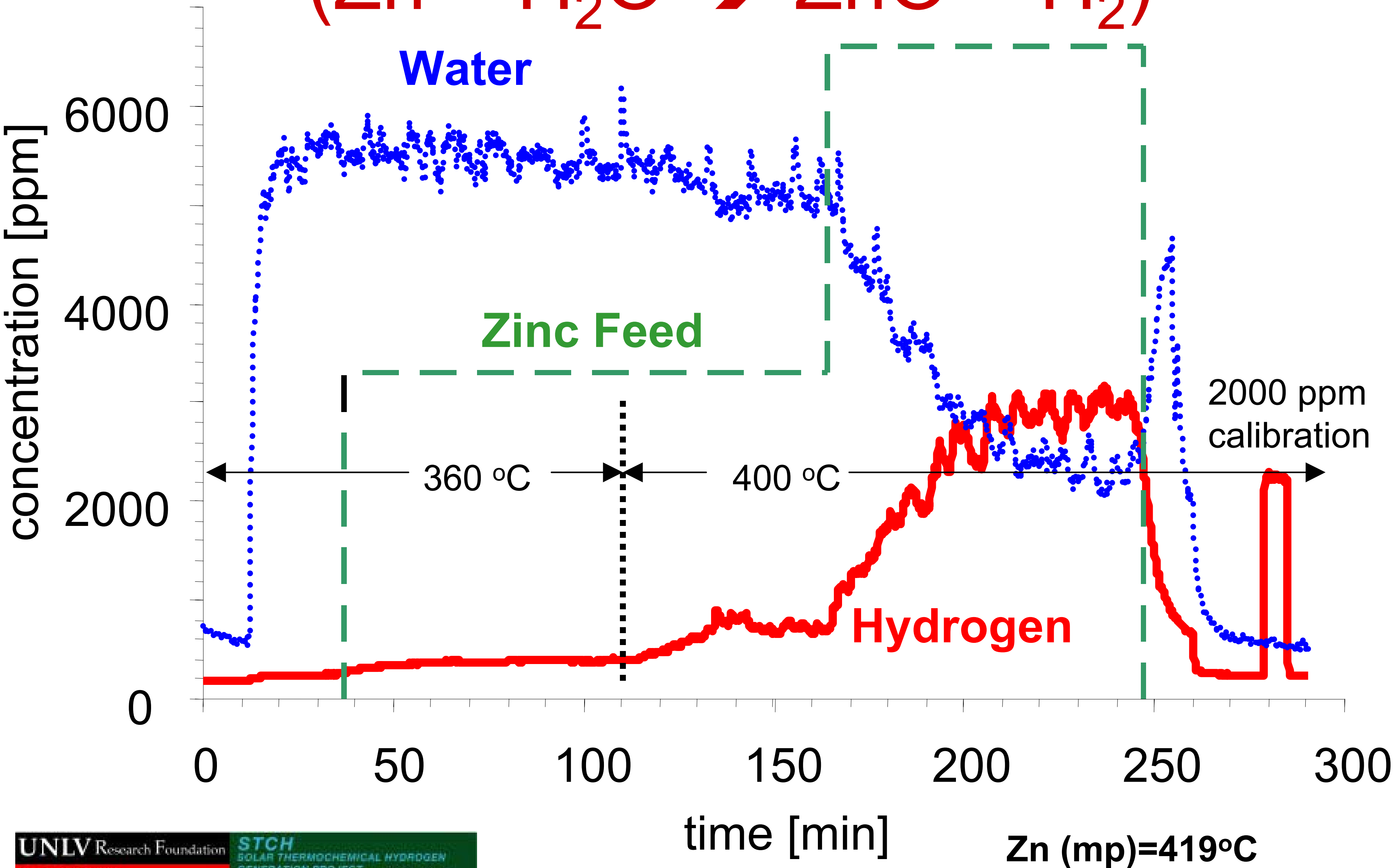


L'vov Theory:

$$E_a = \frac{\Delta H_T^\circ}{\nu} = 362\ kJ/mol$$

$$k_0 = \overline{B}\frac{a\gamma}{F^{\nu^{-1}}} e^{\frac{\Delta S_T^\circ}{R\nu}} = 9.2 \times 10^6 s^{-1}$$

Hydrogen Production from Zn ($Zn + H_2O \rightarrow ZnO + H_2$)



Zn (mp)=419°C

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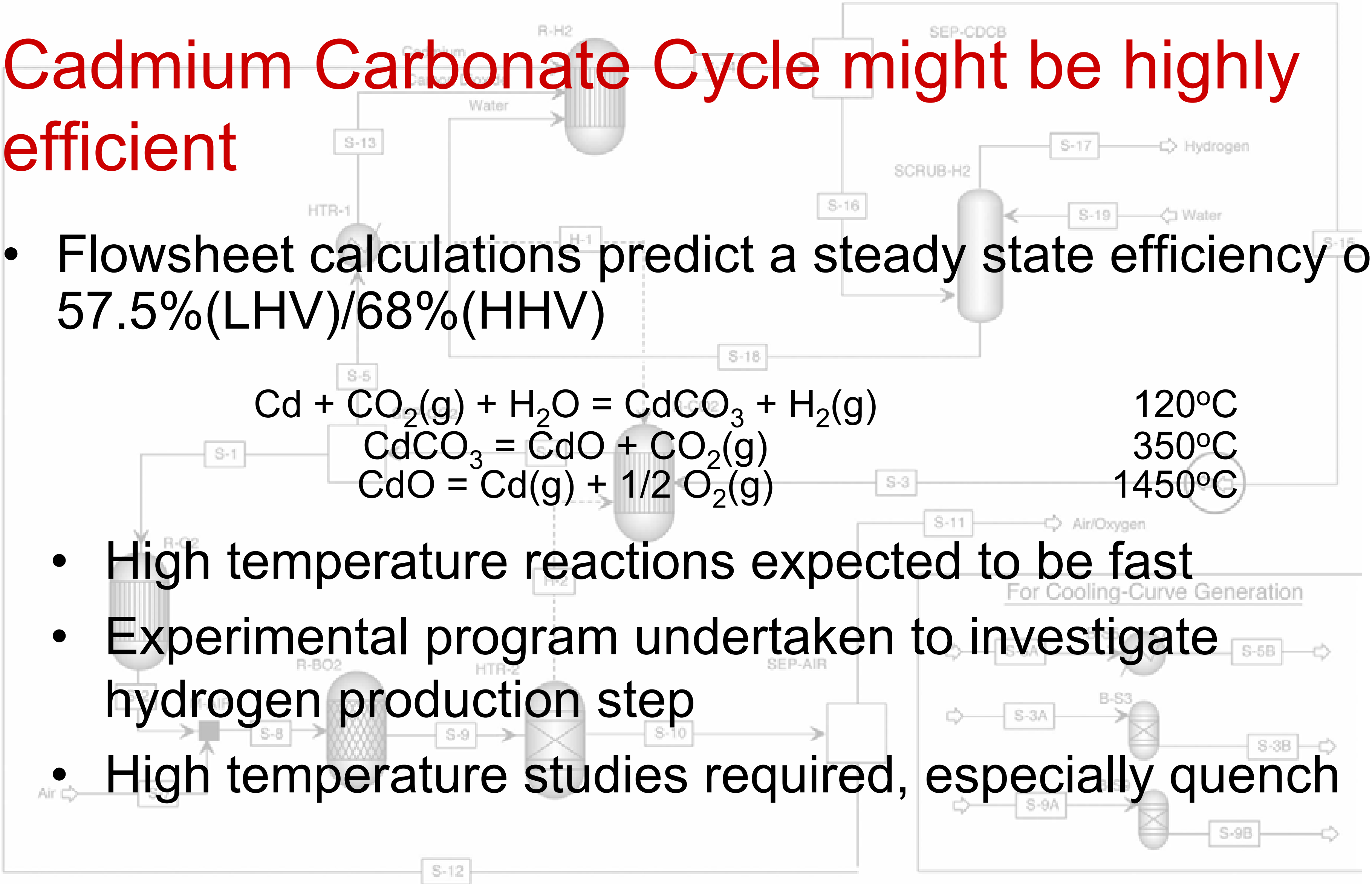
Cadmium Carbonate Cycle might be highly efficient



- Flowsheet calculations predict a steady state efficiency of 57.5%(LHV)/68%(HHV)

$Cd + CO_2(g) + H_2O = CdCO_3 + H_2(g)$ 120°C

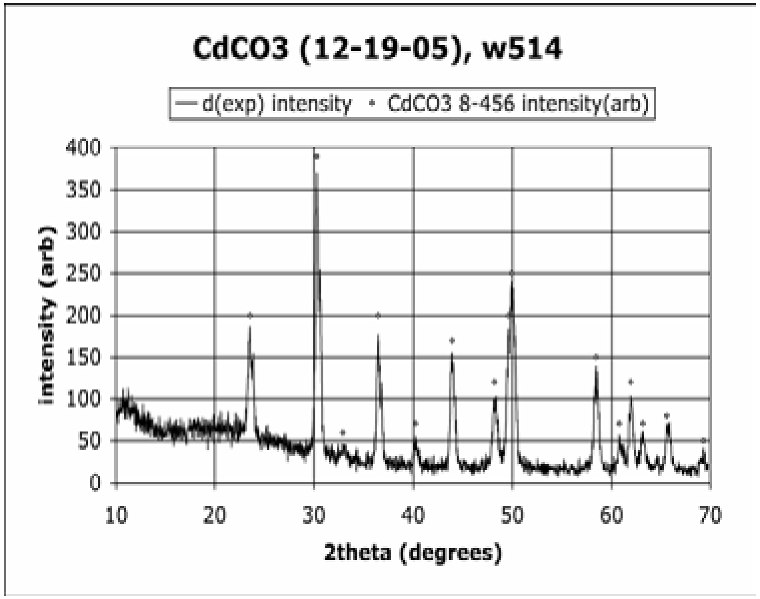
$CdCO_3 = CdO + CO_2(g)$ 350°C

$CdO = Cd(g) + 1/2\ O_2(g)$ 1450°C

  - High temperature reactions expected to be fast
  - Experimental program undertaken to investigate hydrogen production step
  - High temperature studies required, especially quench

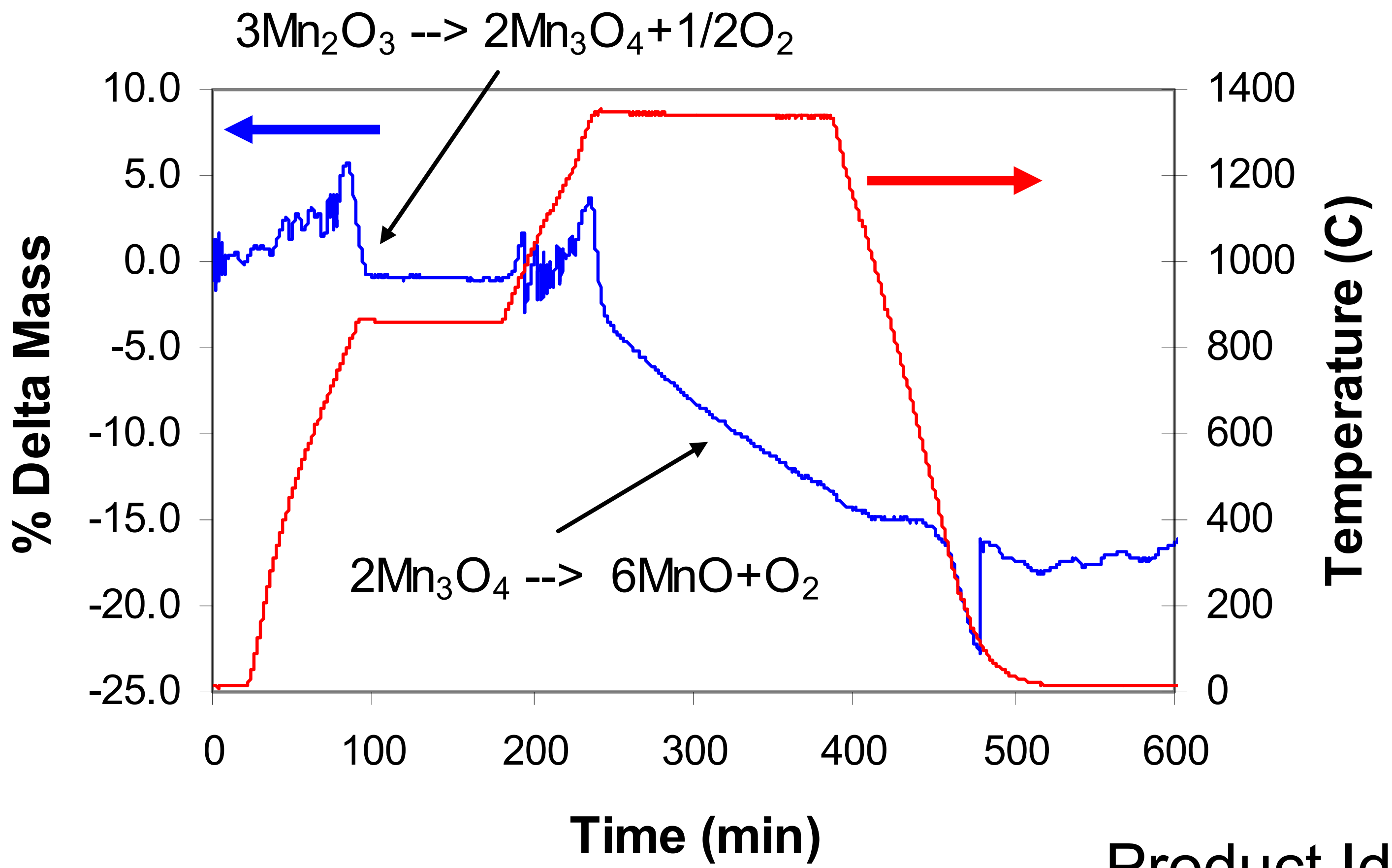
Hydrogen Generated with Ammonia "Catalyst"

- No hydrogen detected without a catalyst
- Ammonia, supplied as NH_4HCO_3, promotes hydrogen generation
  - Mechanism probably involves a $Cd(NH3)_n^{+2}$ complex
  - Gas phase products determined by mass spectrometry
  - Final solid product is $CdCO_3$
- Kinetics being studied
  - No significant change in hydrogen generation rate between 80 and 140°C for large particle Cd
  - Small particle studies underway



Sodium Manganese Cycle

(500 mtorr TGA run @ 1310 °C)

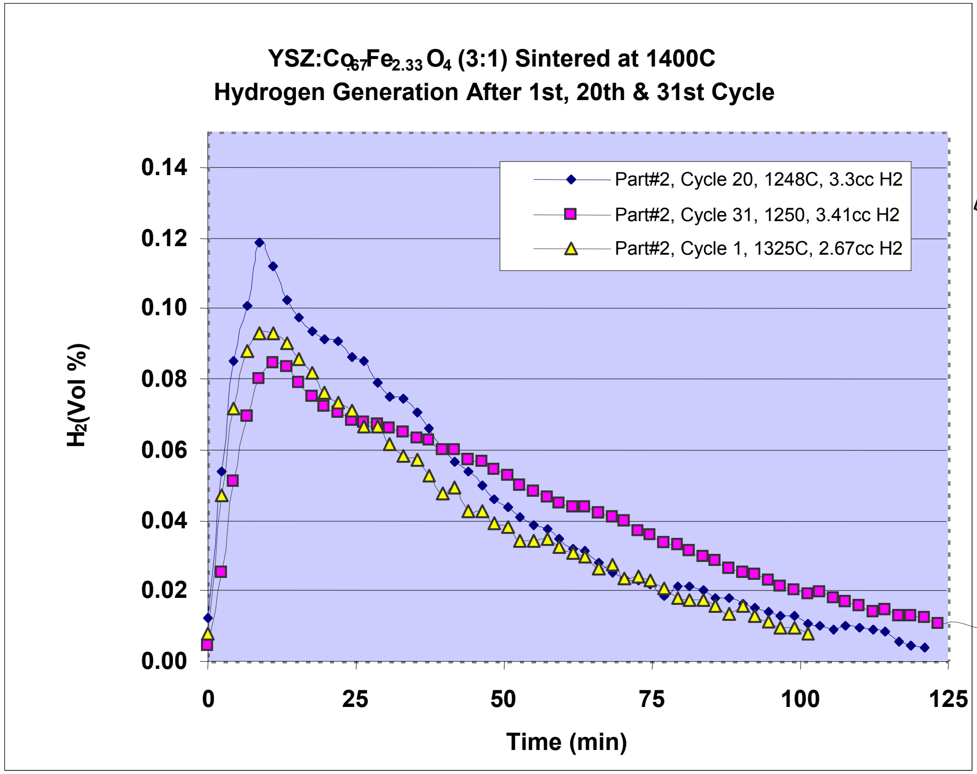


$3Mn_2O_3 \rightarrow 2Mn_3O_4 + 1/2O_2$

$2Mn_3O_4 \rightarrow 6MnO + O_2$

Product Identified as MnO

Cast YSZ: Cobalt-Ferrite Lattice Demonstrates Repeatable Hydrogen Production



Test data showing repeatable hydrogen production over 31 cycles

Co-Ferrite lattice structure after 31 cycles

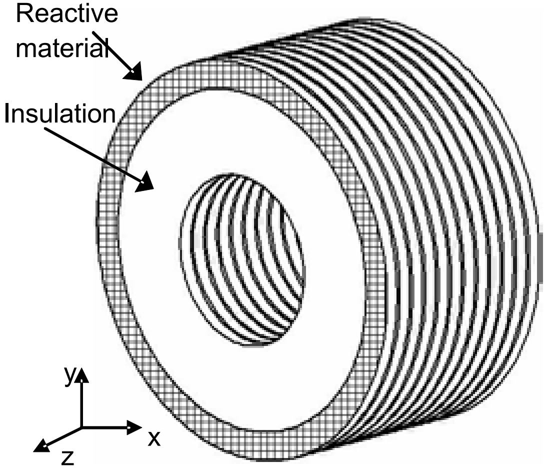
<u>*Current Ferrite Activities*</u>

- Evaluate reaction kinetics with on-sun testing
- Optimize reactive material composition
- Perform additional durability testing and characterization

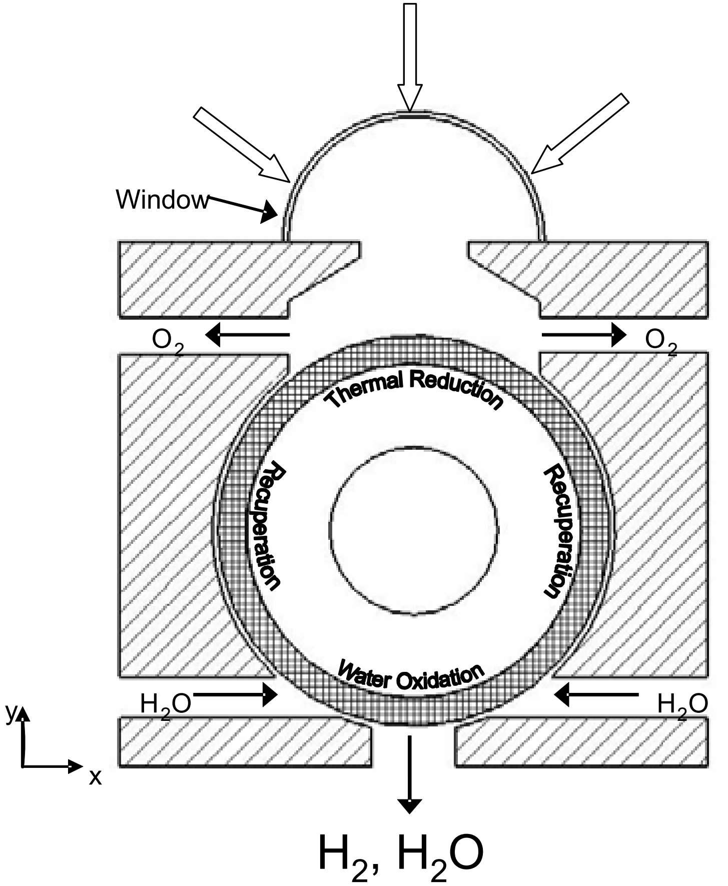
Counter Rotating Ring Receiver Reactor Recuperator (CR5) Thermochemical Engine

Sandia -Invented device uses recuperation of sensible heat to efficiently produce hydrogen in a two-step TC process

Set of counter rotating rings



Concentrated solar flux



Hybrid Copper Chloride Progress

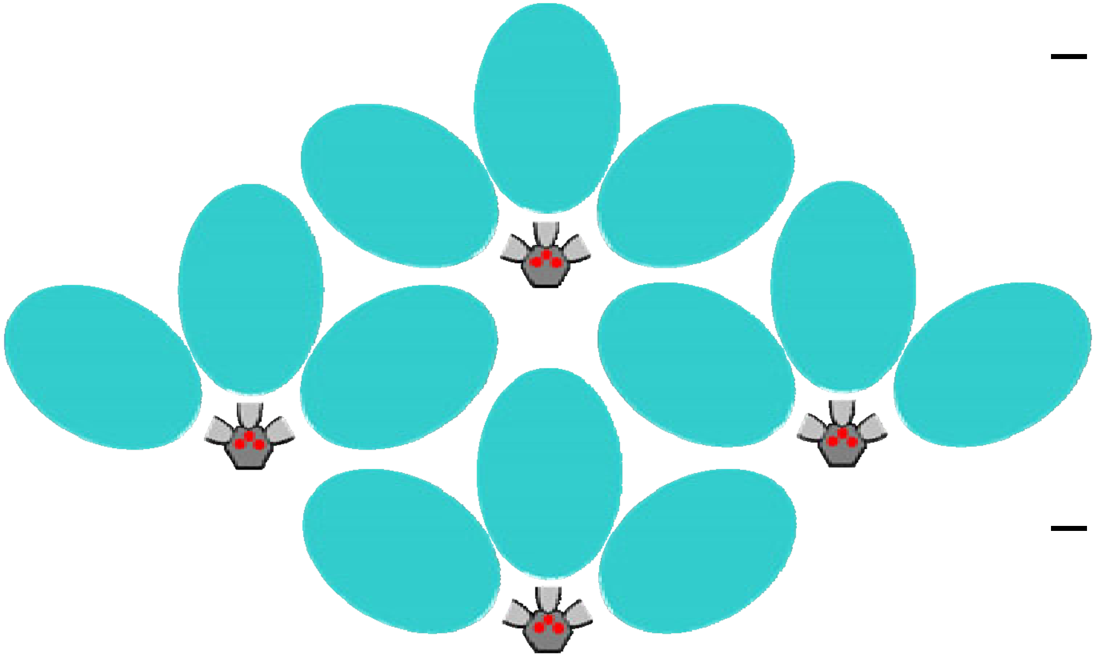
Proof of principle demonstrated for all steps in the reaction:

$2Cu + 2HCl(g) \rightarrow H2(g) + 2CuCl$ (425°C)
$4CuCl \rightarrow 2Cu + 2CuCl_2$ (electrochemical)
$2CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2HCl(g)$ (325°C)
$Cu_2OCl_2 \rightarrow 2CuCl + 1/2O_2(g)$ (550°C)

Low temperature Cu-Cl cycle showed promising efficiency (~40% LHV),but some critical data must be determined experimentally

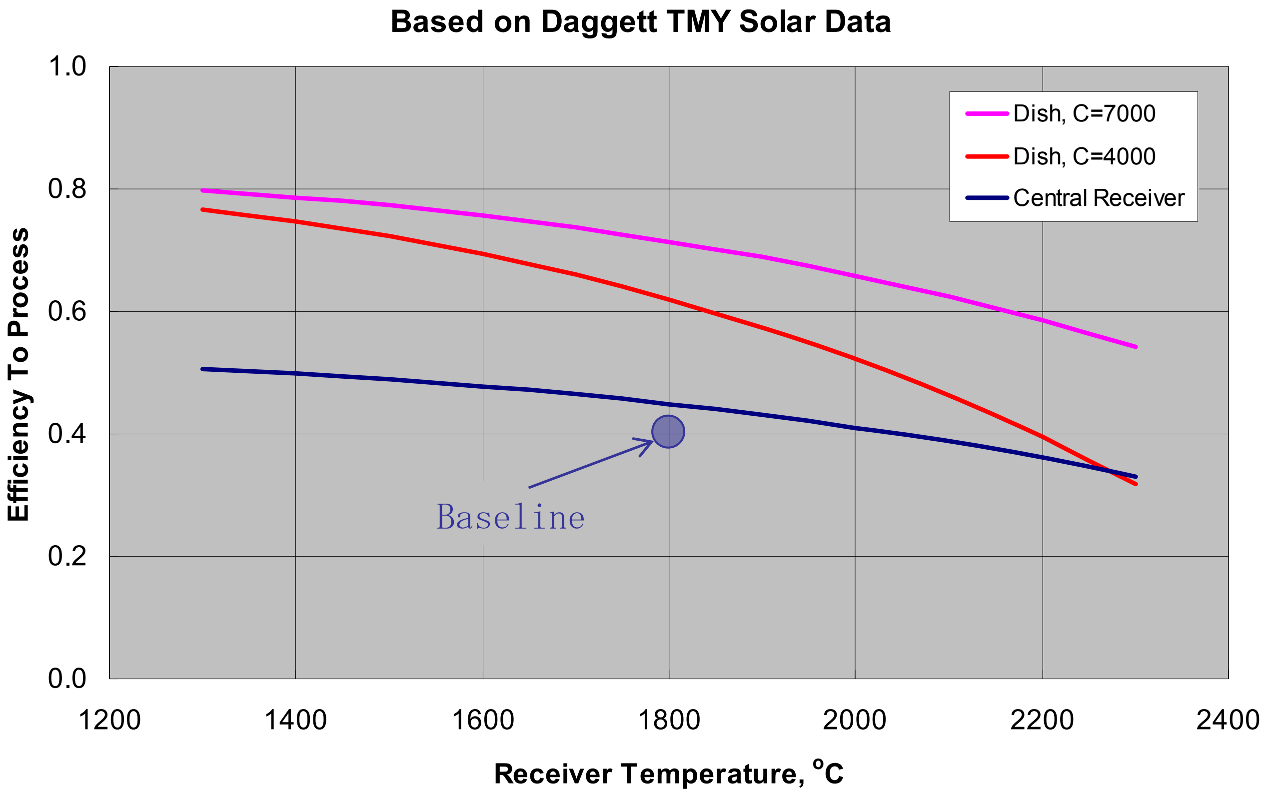
Ultra-High Temperature Advanced Tower Concept

Multiple Field & Secondary/Tower, Single Reactor/Tower



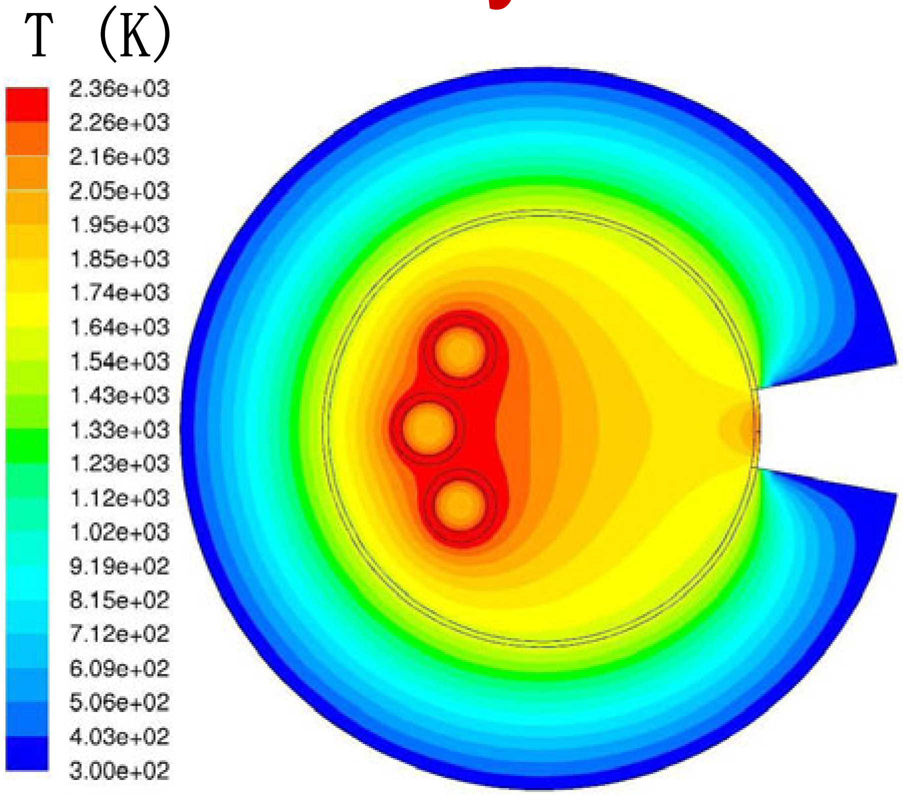
- Baseline System
  - 200m Tower
  - 100m^2 heliostats
    - 358 per field
    - 3 elliptical fields/tower
    - 3 focal lengths/field
    - $\rho = 0.92$
    - $\sigma_{\text{slope}} = 1.3$ mrad
  - CPC Secondary
    - 23.5° acceptance angle
    - $C_{\text{geometric}} = 6.1$
  - Design, size and performance of secondary can be improved with further optimization

Annual Solar Performance



- Yearly Direct Daggett: 2787 kWhr/m^2 (2679 kWhr/m^2 available)
- Yearly Delivered: 1990 kWhr/m^2
- Annual Energy Delivered (to drive process): 259 MWhr/tower
- Economies of scale for reactor/process components and infrastructure provide significant cost advantage to advanced tower over dish systems for large scale plants

Preliminary Solar Receiver Concept



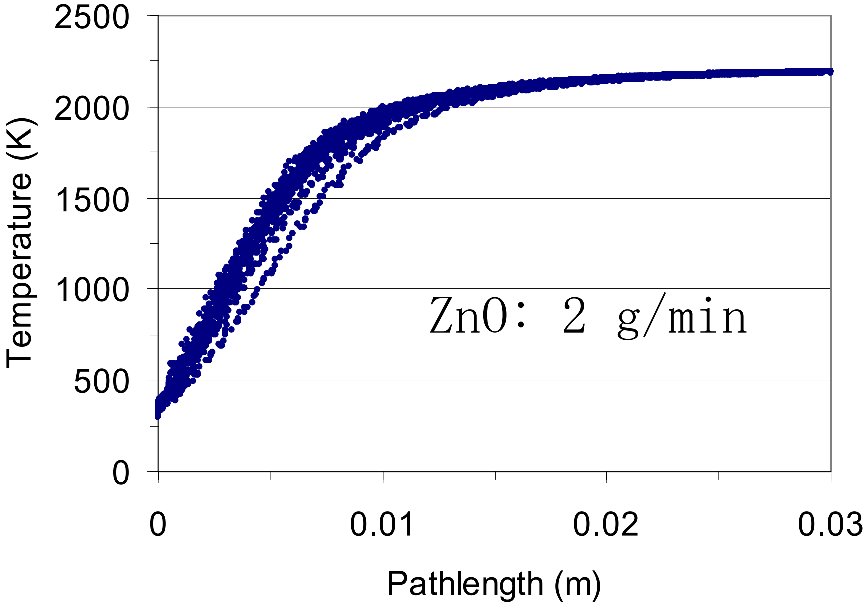
8000 W (3000 suns)

T_{max} = 2341 K

T_{ave} = 2107 K

X = 60.3%

ZnO: 80 g/min



Particle temperature along the tube with higher temperatures closer to the tube wall

(to be tested)

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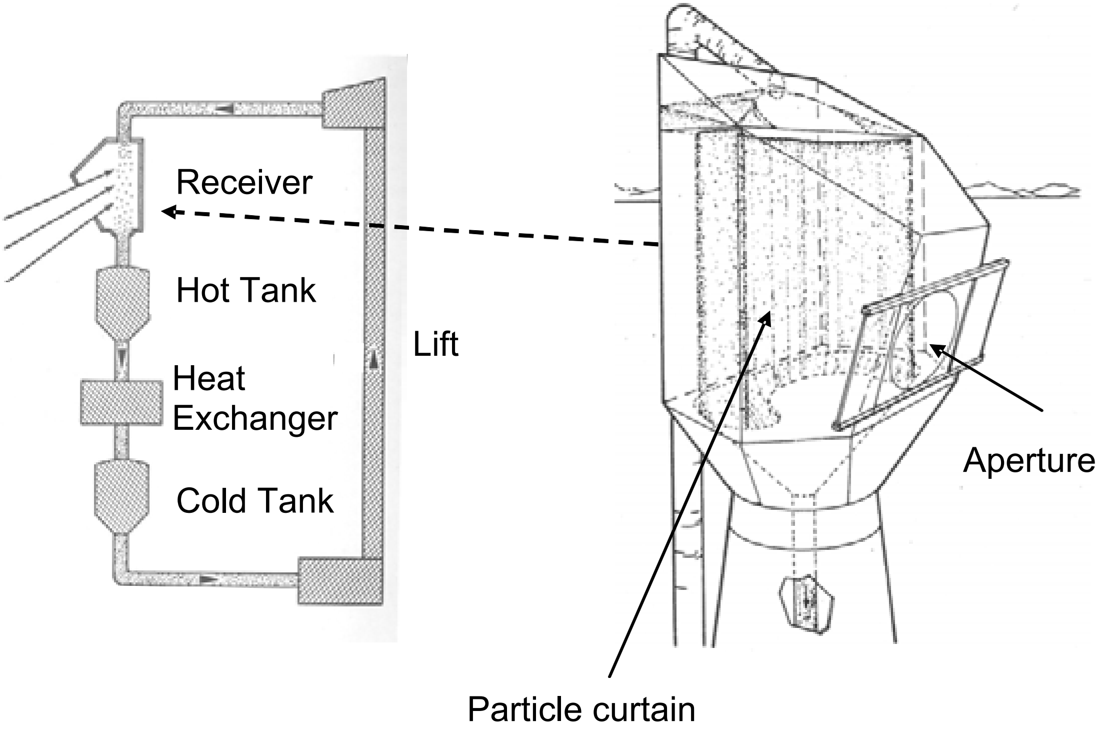
Solid Particle Advanced Solar Receiver for Thermochemical Processes



Receiver

Hot Tank

Heat Exchanger

Cold Tank

Lift

Aperture

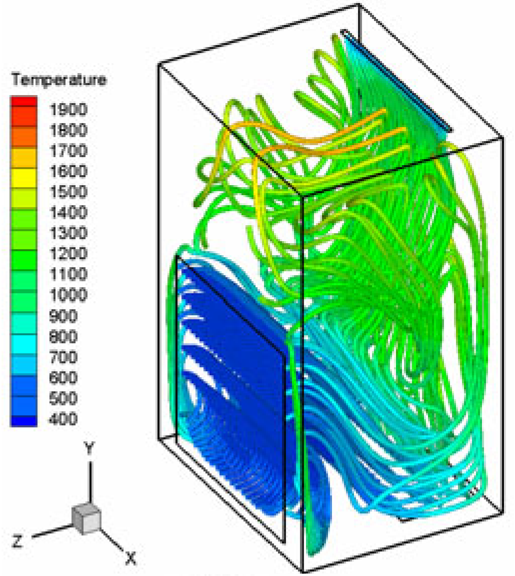
Particle curtain

- The solid particle receiver can achieve temperatures in excess of 950 °C
- Falling ceramic particles are directly heated by concentrated solar energy
- The complete solar interface includes two-tank storage and particle lift as well as a heat exchanger to couple the receiver to the thermochemical process

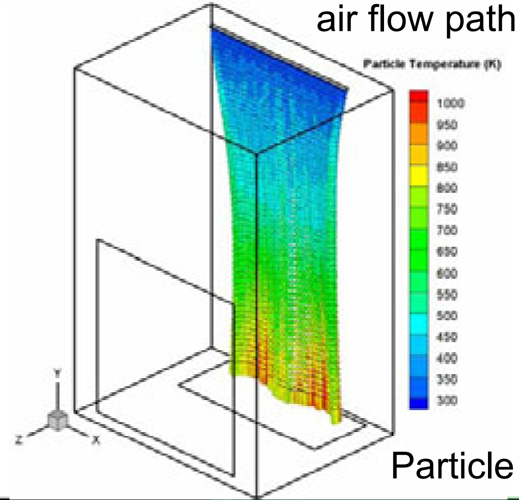
-Completed first level component design

-Began cold flow testing

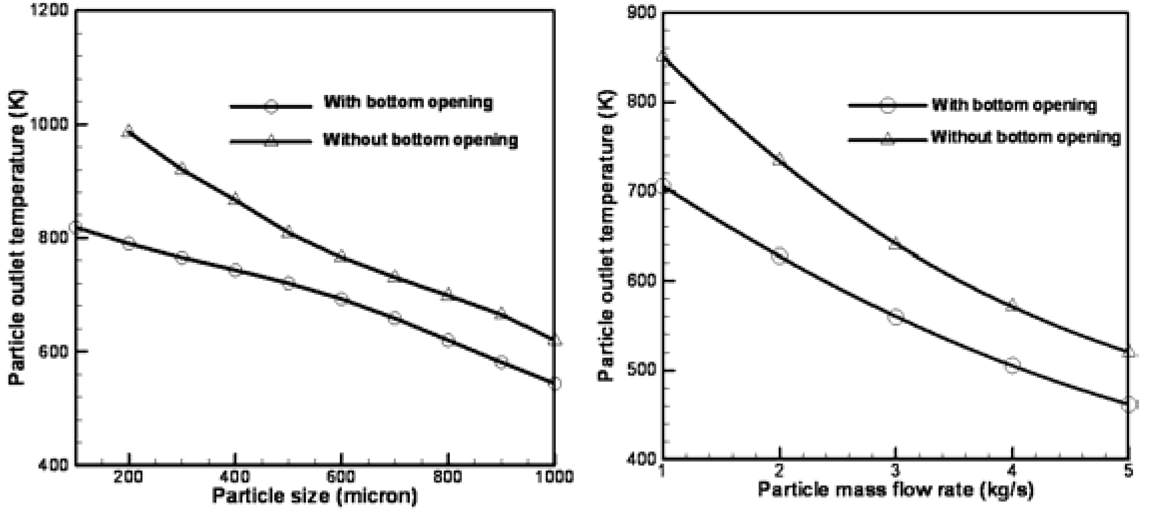
CFD Analysis
- Solid Particle Solar Receiver



air flow path lines



Particle track



Cavity efficiency as a function of particle size and particle mass flow rate.
Solar irradiation flux : 920 kw/m2

- Operating condition for high outlet particle temperature (sulfur-iodine thermochemical process, Particle temperature >1200 K)
- Decreasing the mass flow rate
- Enlarging the particle size
- Increasing the solar irradiation flux

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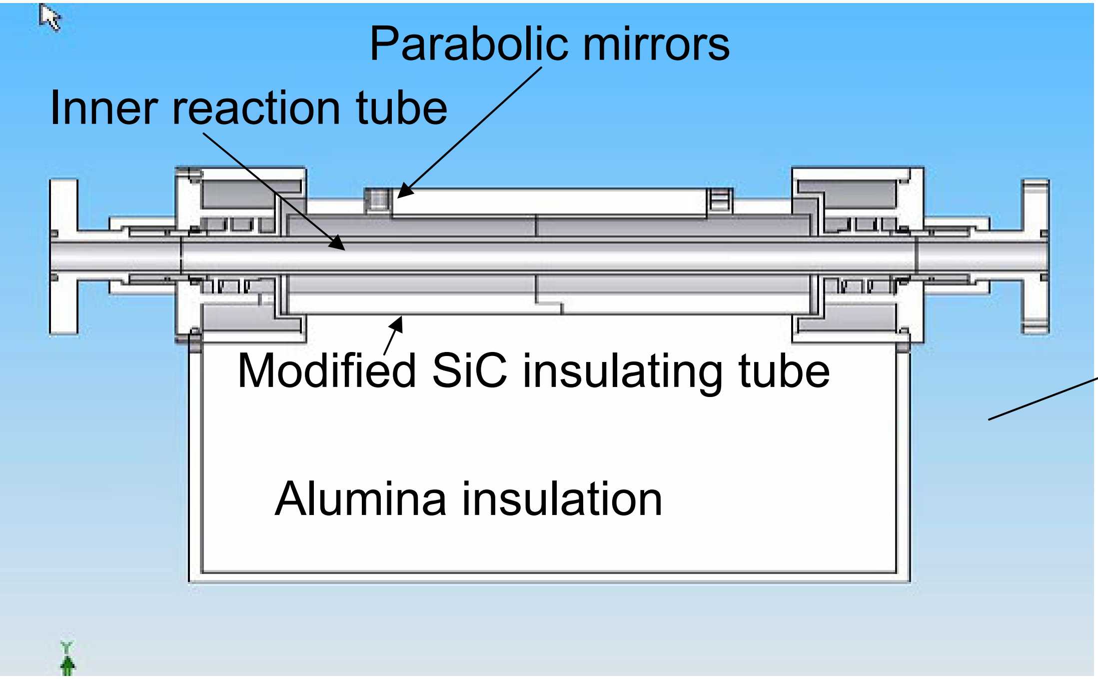
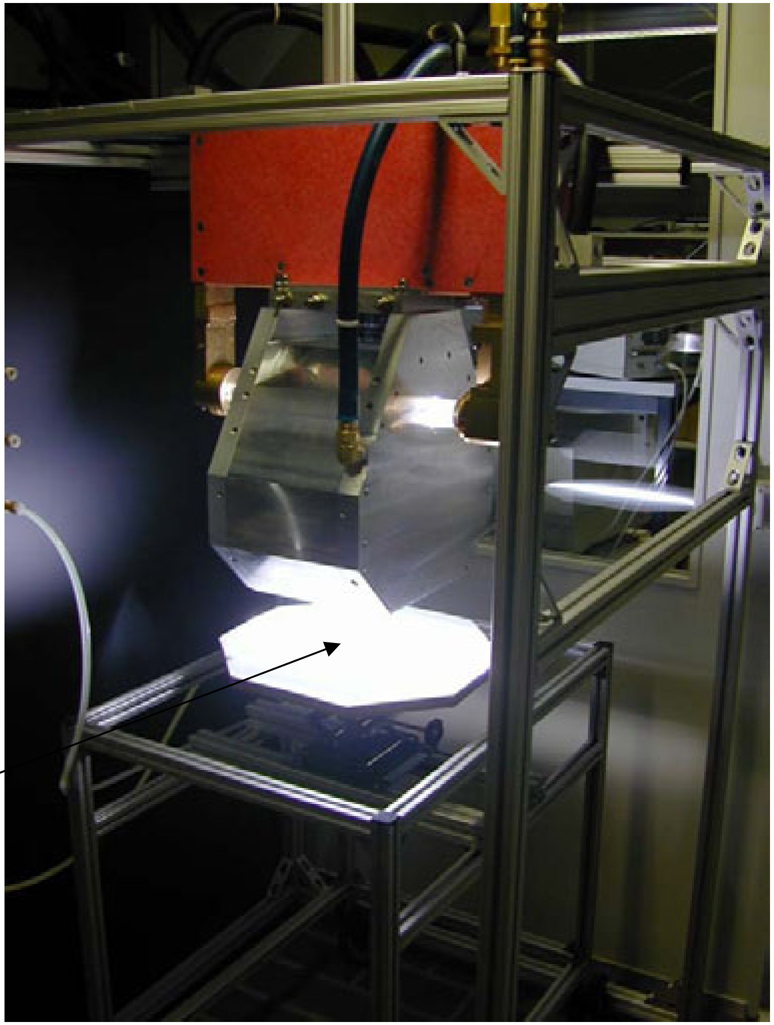
High Flux Solar Simulator

Windowless Tubular Receiver





ETH-Zurich Solar Simulator

Future Work

- Experimentally resolve the uncertainties of the down selected cycles; close cycles
- Optimize system design for various temperatures and power requirements
- Develop and validate the transport mechanisms and the design of the solid particle receiver
- Update H2A process economics
- Investigate materials challenges for solar receiver and other system components