Solar Cadmium Hydrogen Production Cycle

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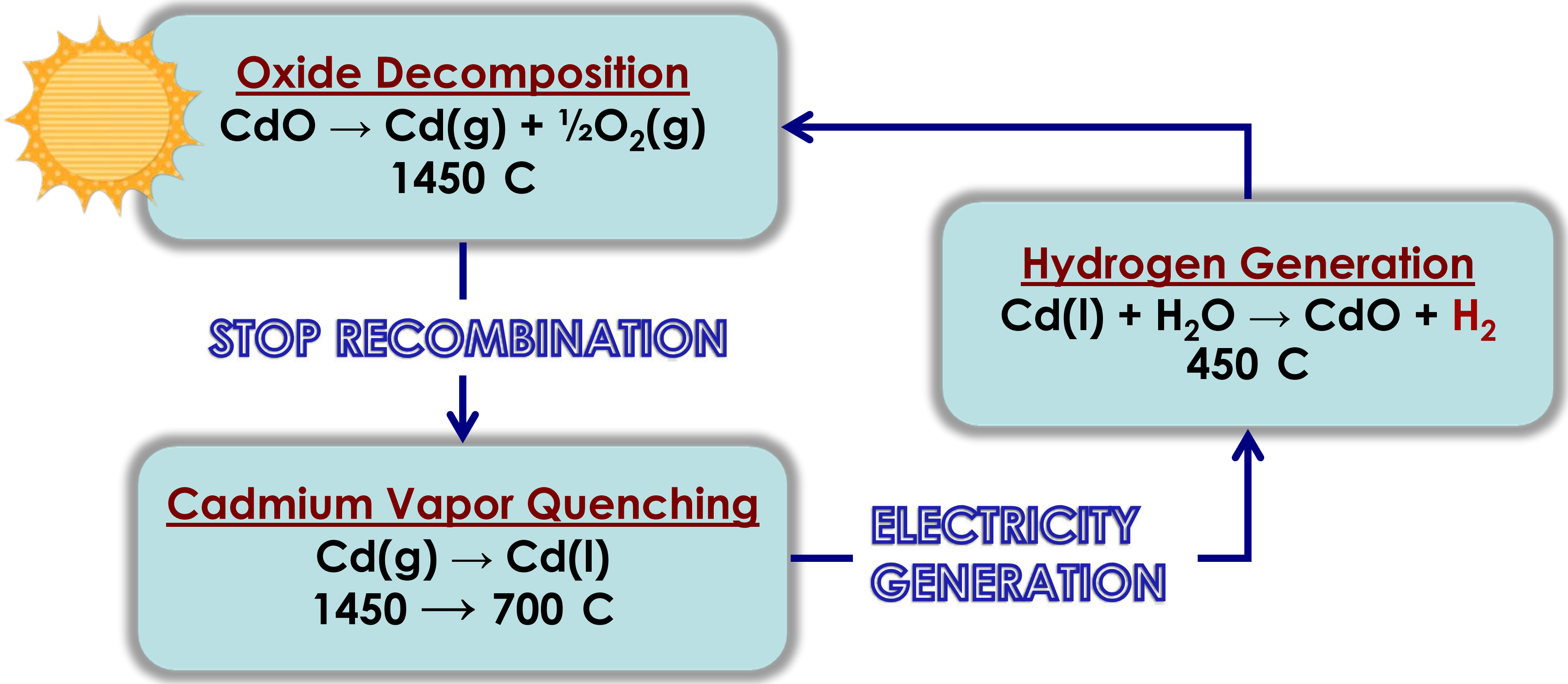
The solar cadmium-hydrogen cycle has a calculated efficiency of 59% (LHV)



- ➢ Cycle has no waste effluent
- ➢ Only heat and water are required as inputs

Overview

Timeline

Start Date: Jan 2006

End Date: Oct 2009

95% completed

Budget

DOE Total: $1.26M

GA Total: *$0.49M*

FY08: $380K (*$197K*)

FY09: $210K (*$110K*)

Barriers

U. High Temperature Thermochemical Tech.

V. High-Temperature Robust Materials

X. Coupling Concentrated Solar Energy and Thermochemical Cycles

Partners

University of Nevada, Las Vegas

Project Objectives and Approach

To demonstrate the feasibility and economics of a solar cadmium hydrogen cycle

- **Validate the key reaction steps with experiments**
- **Establish design concepts for process steps based on experimental data**
- **Integrate process design concepts and solar field design into a flowsheet for a solar hydrogen plant**

Metric	Unit	2008	2012	2017
H_2 cost	\$/kg H_2	10.00	6.00	3.00
Efficiency (LHV)	%	25	30	>35

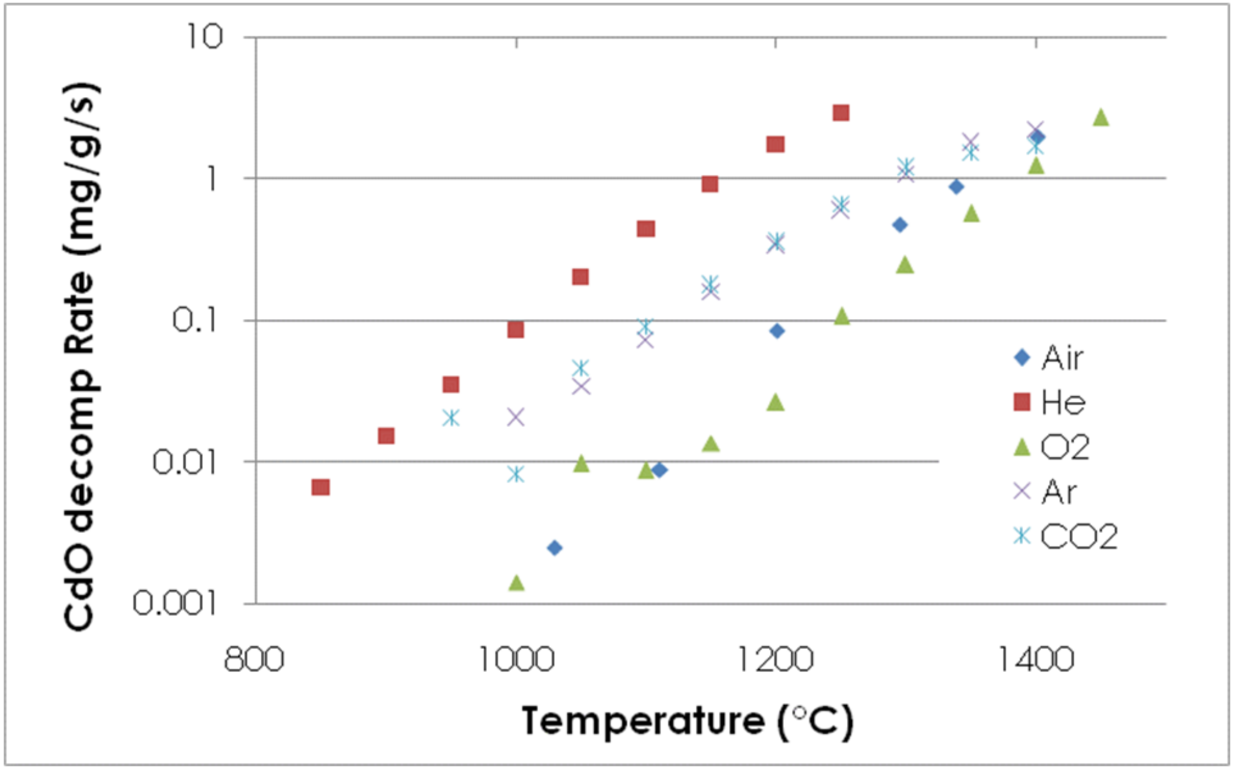
Technical Approach

CdO decomposition	➢ Determine the decomposition kinetics under various carrier gases
Cd vapor quenching	➢ Measure the Cd-O_2 vapor reaction rate and determine the required quench rate ➢ Determine via modeling if quenching is practical
H_2 generation	➢ Applied mechanical and chemical means to achieve fast hydrogen generation kinetics
Economics	➢ Design flowsheet using most probable process routes ➢ Design solar field, reactor and plant ➢ Integrate hydrogen and solar plant for H2A analysis

Milestones and Accomplishments

Milestone	Accomplishments	%Comp
Demonstrate CdO decomposition	➢ Effect of carrier gas on decomposition kinetics established ➢ Sub 1150°C decomposition demonstrated	100
Measure Cd-O_2 reaction rate	➢ Reaction rate wrt temperature and O_2 concentration measured	100
Demonstrate H_2 generation with Cd	➢ Demonstrated two pathways to use either molten or solid Cd to generate H_2	100
Modeling of Cd vapor quench	➢ Modeling studies of vapor quench on going	50
H2A Analysis	➢ Process flowsheet and solar field design completed ➢ Preliminary H_2 cost established	95

The CdO decomposition rate is a function of carrier gas and temperature

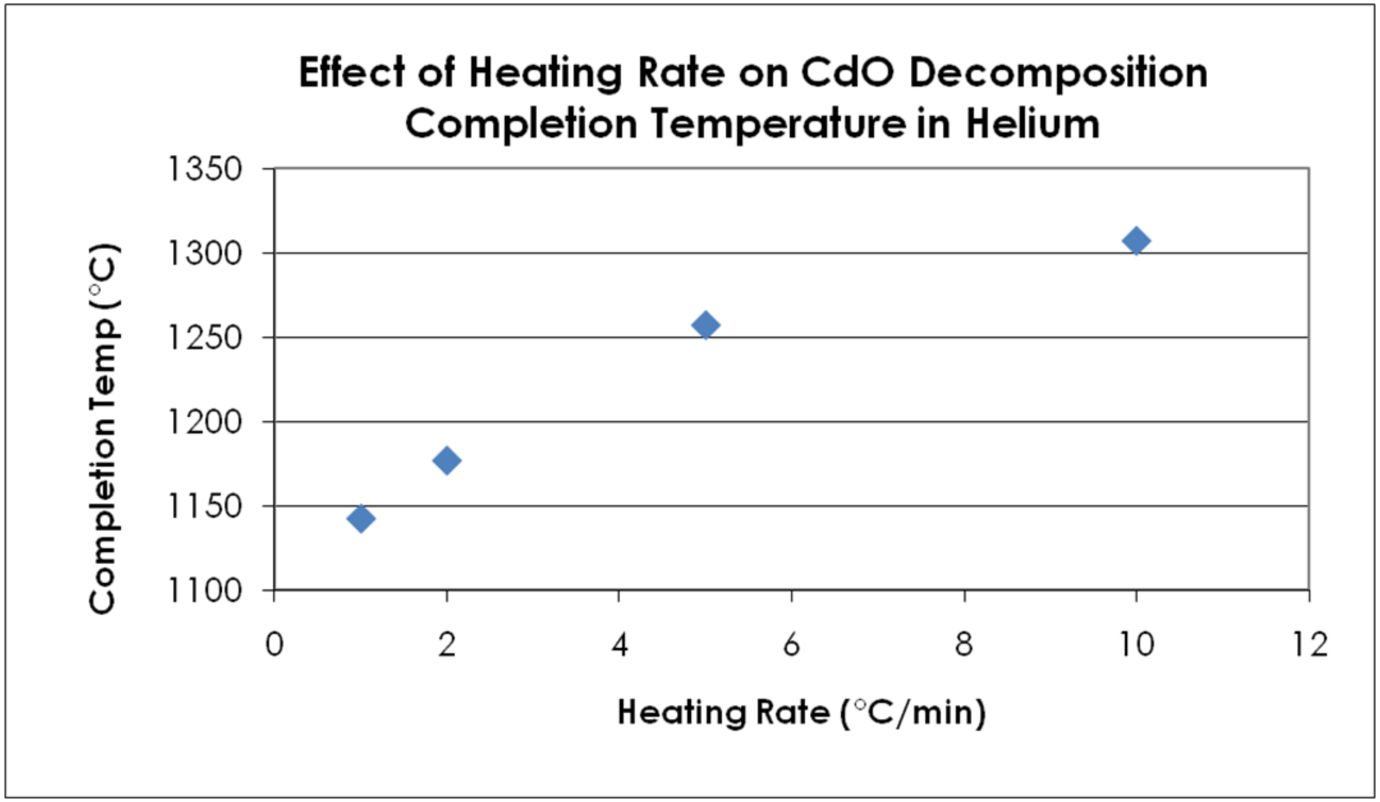


Gas*	D ($10^4 m^2/s$)
He	0.753
Ar	0.220
CO_2	0.214
Air	0.153

*diffusivity of O_2 at room temp

- **The decomposition is controlled by the back reaction and oxygen diffusivity**

CdO decomposition temperature was further reduced with slow heat rate



- **The lower decomposition temperature will reduce solar field requirements**

Decomposition is very sensitive to O_2 diffusivity and back reaction

Gas	*E_a (kJ/mole)*
Ar	**248 ± 6**
He	**241 ± 10**
CO_2	268 ± 8
Air	363 ± 10
O_2	384 ± 4

$$d\alpha/dt = k_o \bullet \exp(E_a/RT) \bullet (1-\alpha)^n$$

Galwey & Brown

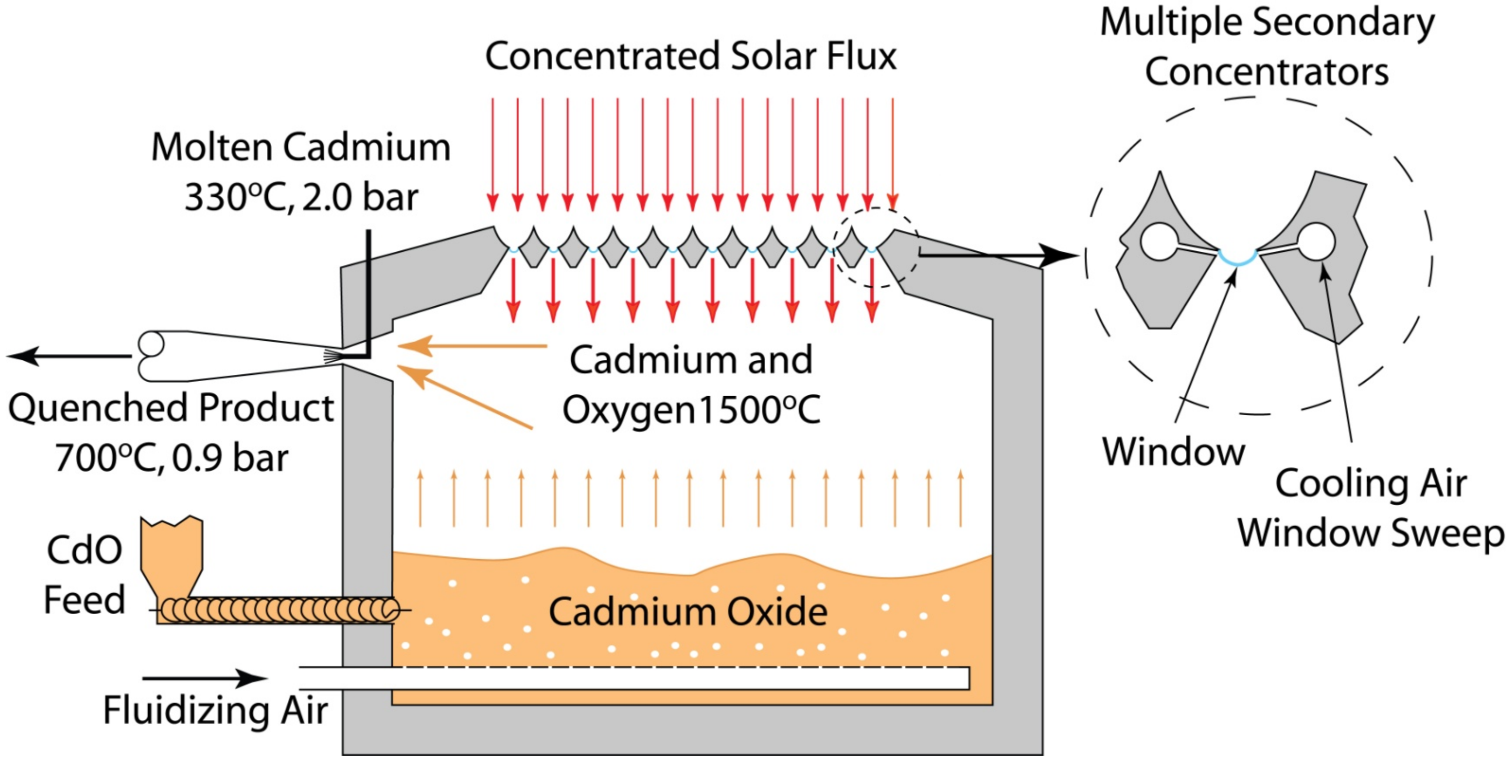
- $CdO(s) \rightarrow Cd(g) + ½O_2(g)$
- Theoretical E_a is 241 kJ/mole
- Back reaction in O_2 rich environment leads to higher apparent E_a

Sample (mg)	*E_a*	*k**
33.6	250.5	**7.48E-01**
65.7	237.3	**9.13E-03**

- E_a is configuration independent
- k* is strongly gas diffusion dependent

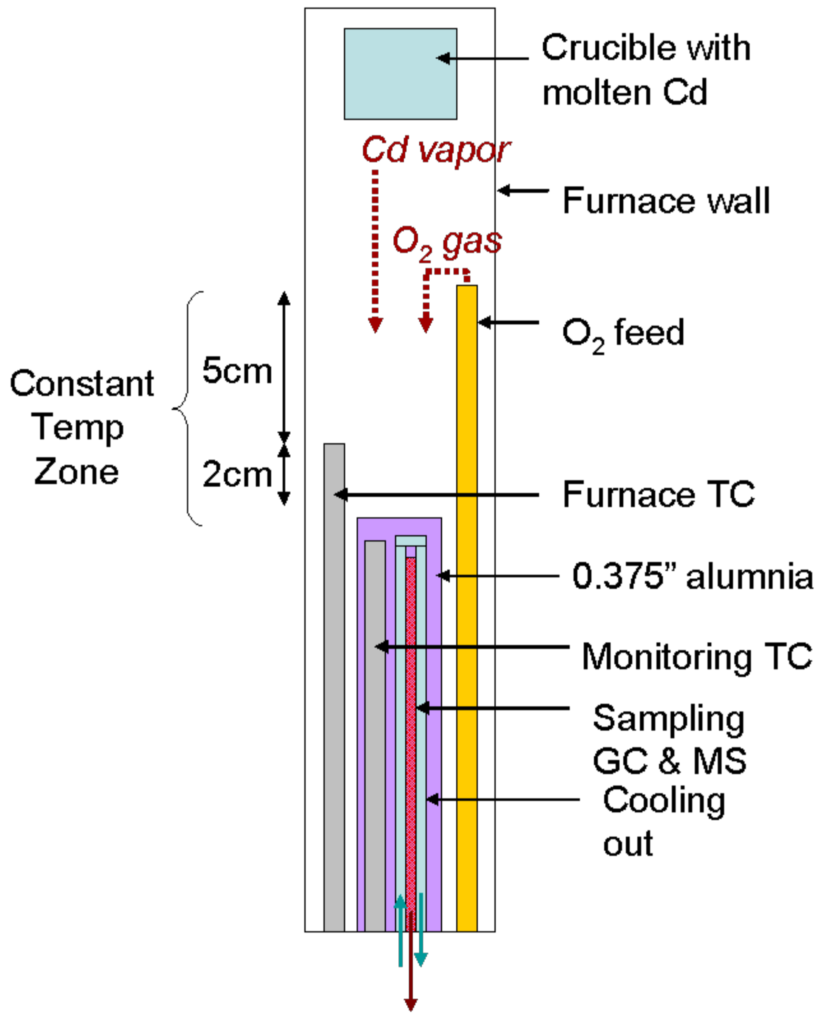
$$k^* = k_o \bullet \exp(E_a/RT_o)$$

CdO baseline decomposer design utilizes a fluidized bed design



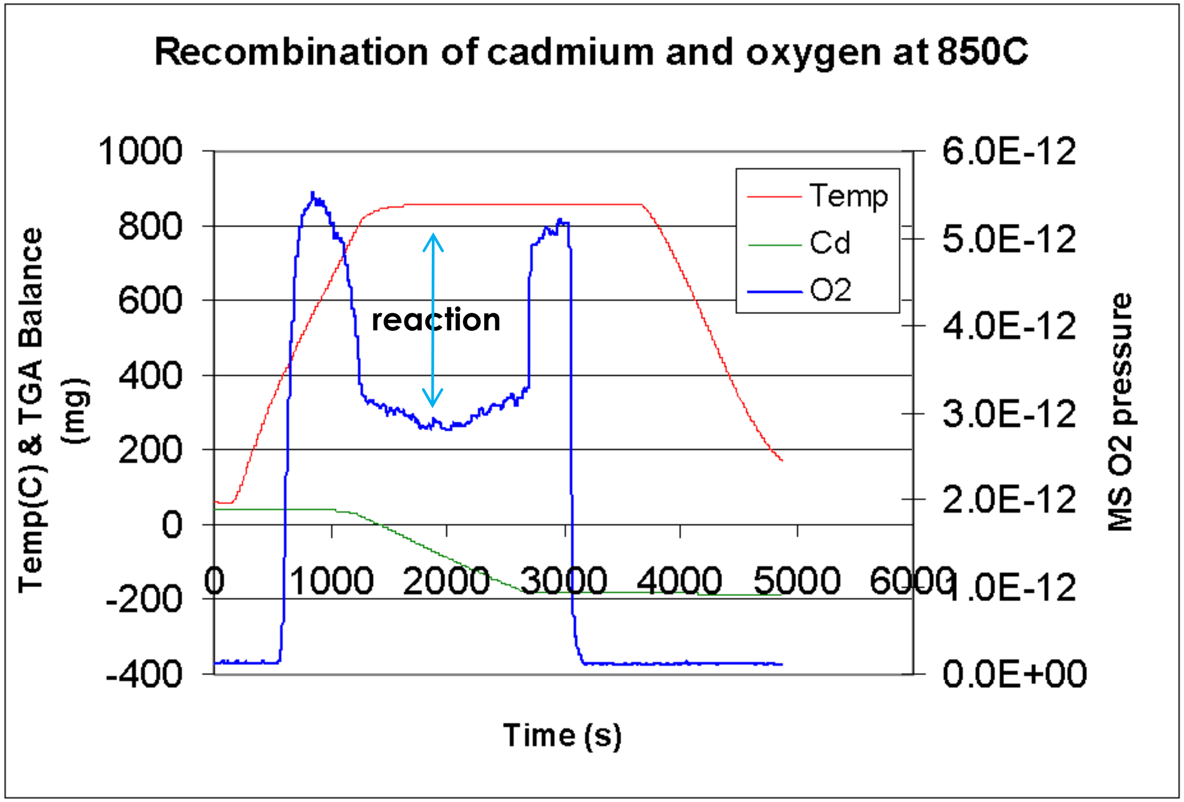
- This design concept fits with a beam down solar tower
- Secondary concentrators and windows are employed
- Atm. air is used as carrier gas to fluidize the particle

The cadmium oxygen reaction rate was measured using a TGA



- **Cd and O_2 flow through the furnace and react**
- **Gases are quenched after the reaction zone**
- **Reaction rate was calculated using:**
  - ***O_2 reduction***
  - ***Cd evap. Rate***
  - ***Time of travel***

A Mass Spec. measures the amount of O_2 that has been reacted



- **Measurements for temperature between 700-1400°C have been made**

The measured reaction rate falls between 1 to 6% Cd reacted per second (800-1400°C)

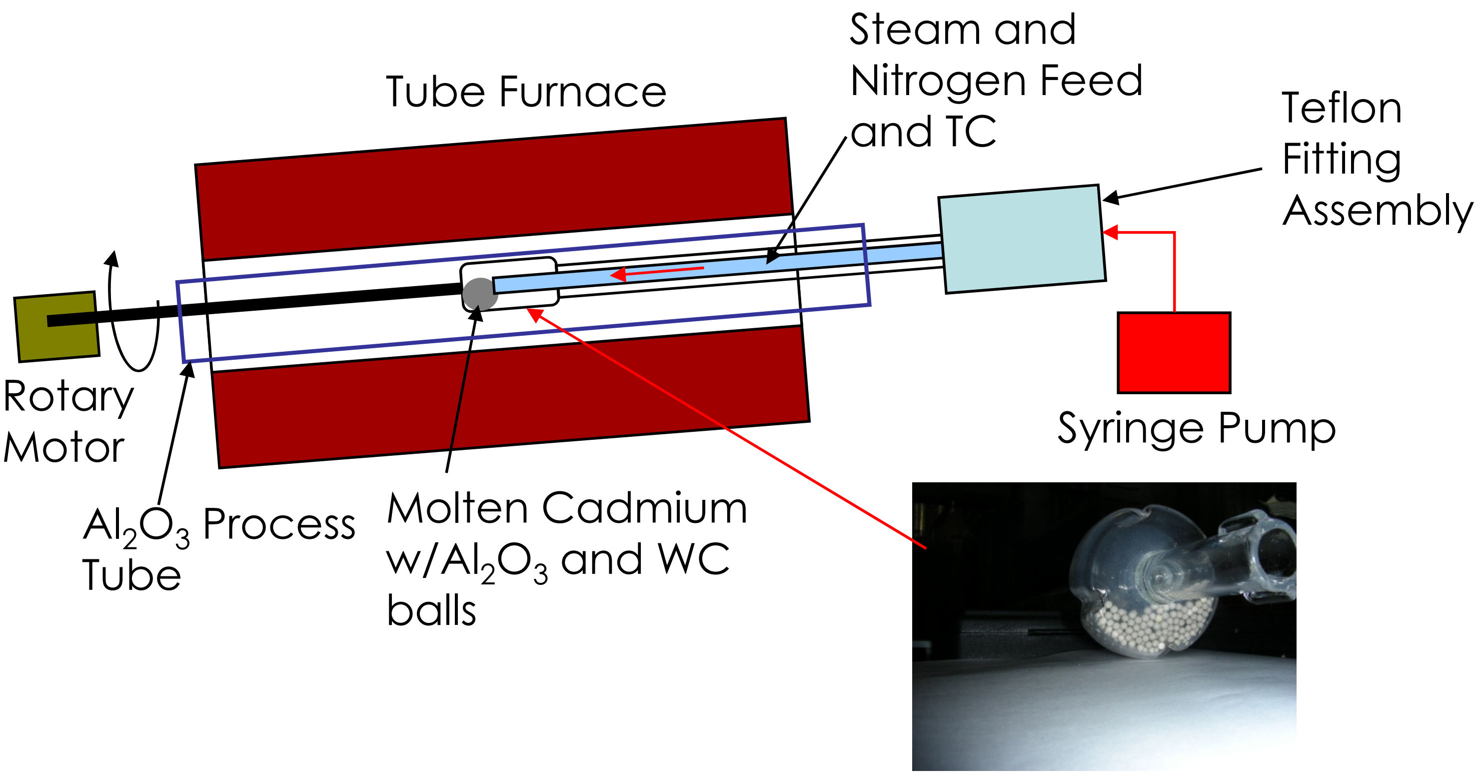
$$rate_F = A_o * \exp(E_a/RT) * P_{O2}{}^{m} * P_{Cd}{}^{n}$$

$$rate_R = A_o * \exp(E_a/RT) * (1/K_{eq}) * P_{O2}{}^{m-1} * P_{Cd}{}^{n-2}$$

$rate_F = rate_R$ at equilibrium

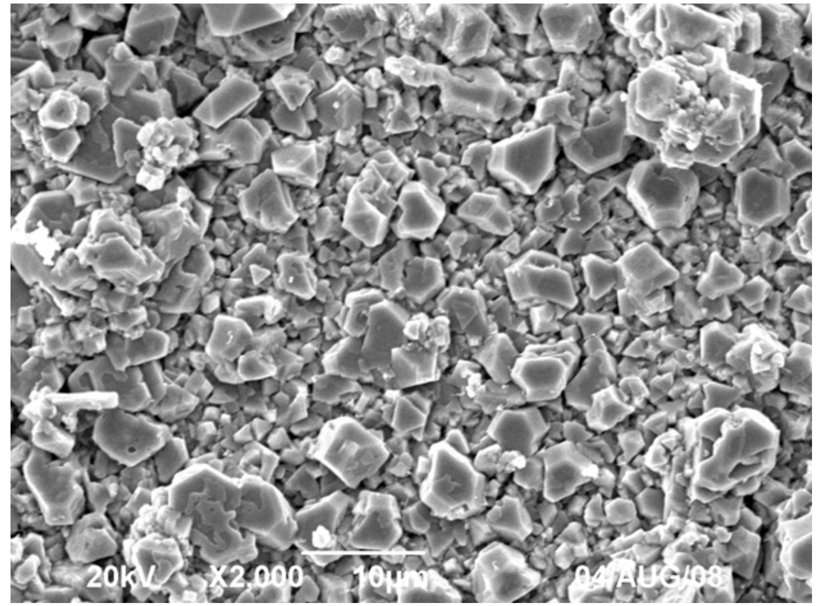
- Preliminary result give best fit with the experimental results at m = 0 and n=0.18
- Model implies Cd and O_2 recombination is not sensitive to the amount of oxygen present
- Modeling of the quench process based on the reaction rate is in progress

A rotary kiln was used for molten Cd hydrolysis to maximize steam-molten contact



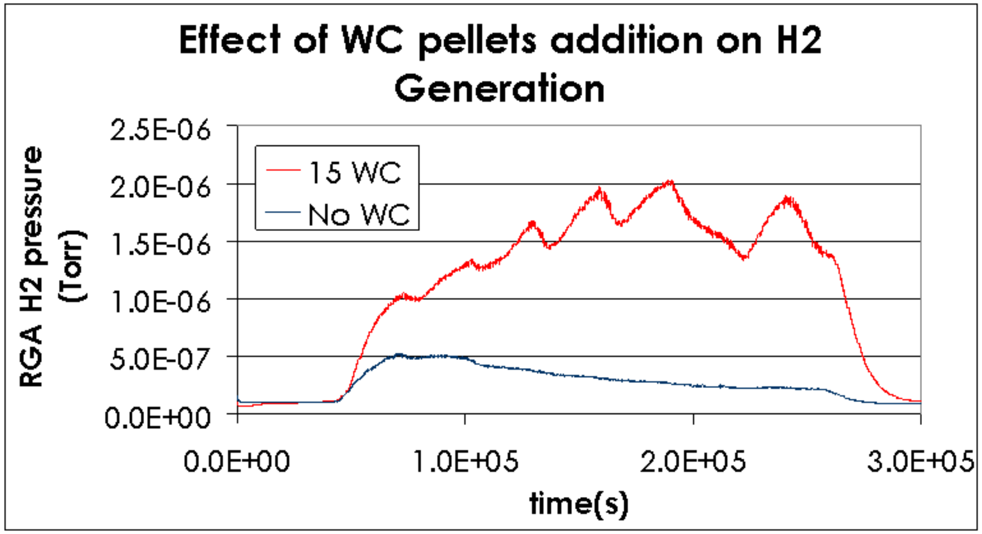
- **WC pellets added to splatter molten Cd to increase surface area**

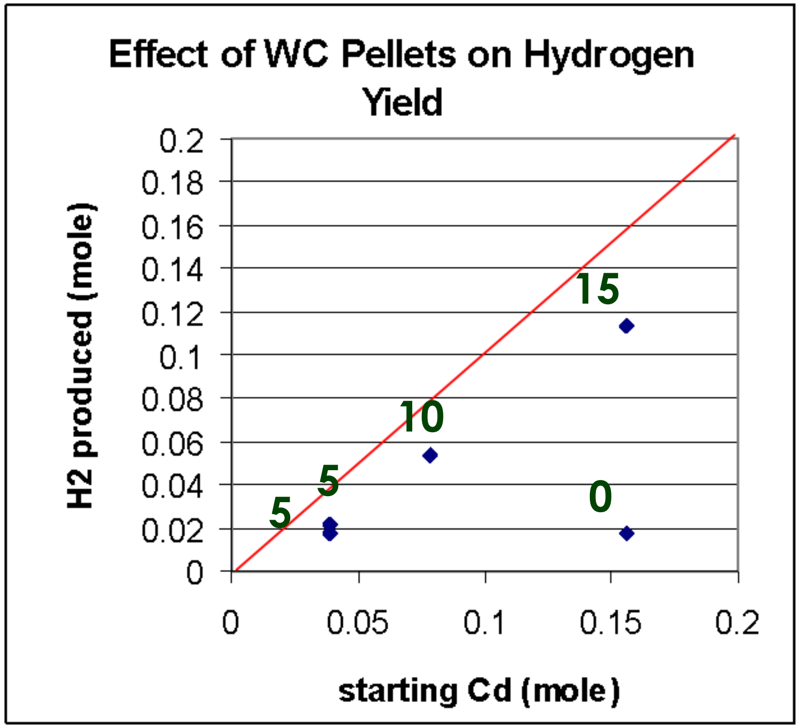
CdO particles formed by the molten Cd-steam reaction ranges from 1 up to 10 microns in size



- CdO particles were carried out of the reactor
- Size range suitable for fluidizing

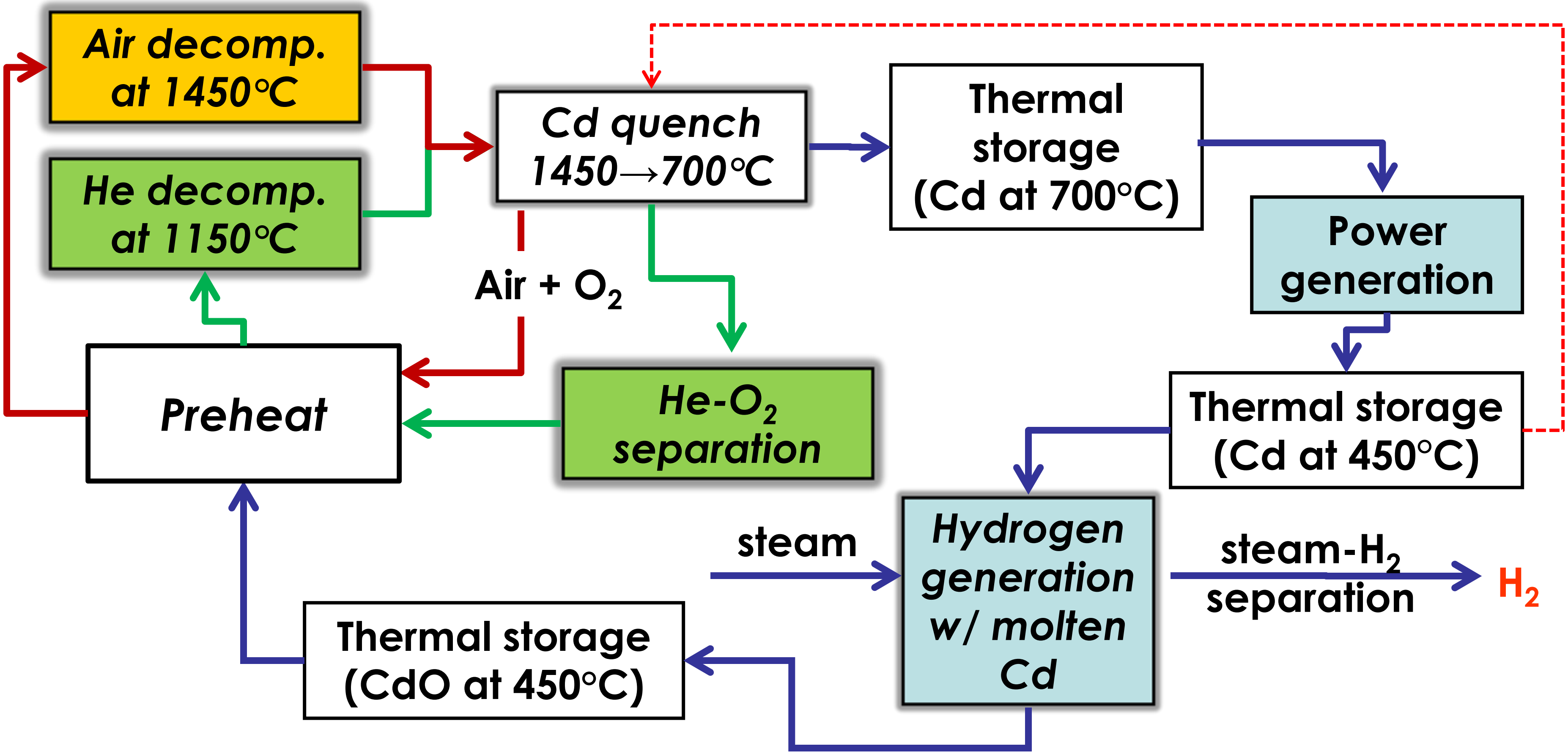
Hydrogen yield is enhanced by increasing the surface area of cadmium for reaction





- Theoretical steam to H_2 conversion of 3% can be achieved by using a pressurized rotary kiln with means to maximize cadmium-steam contact

Baseline flowsheet using air as carrier gas has been established (Efficiency 58% LHV)

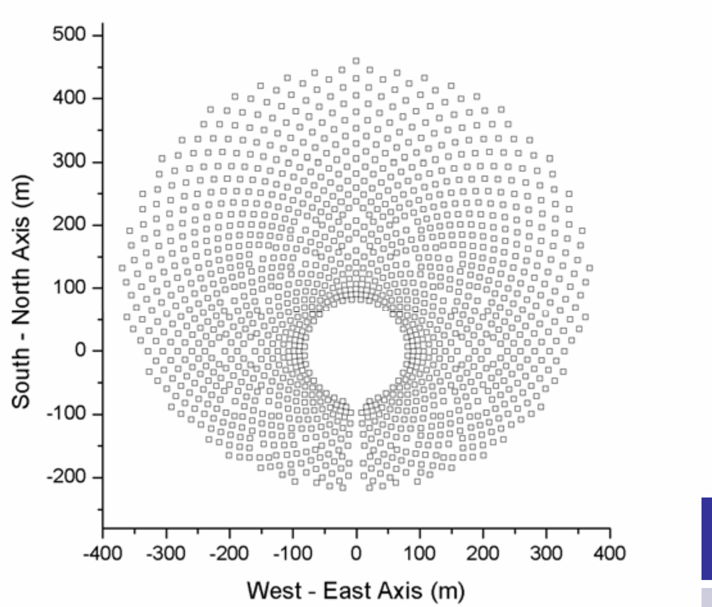


On Sun Hours: CdO decomposition and Cd vapor quench

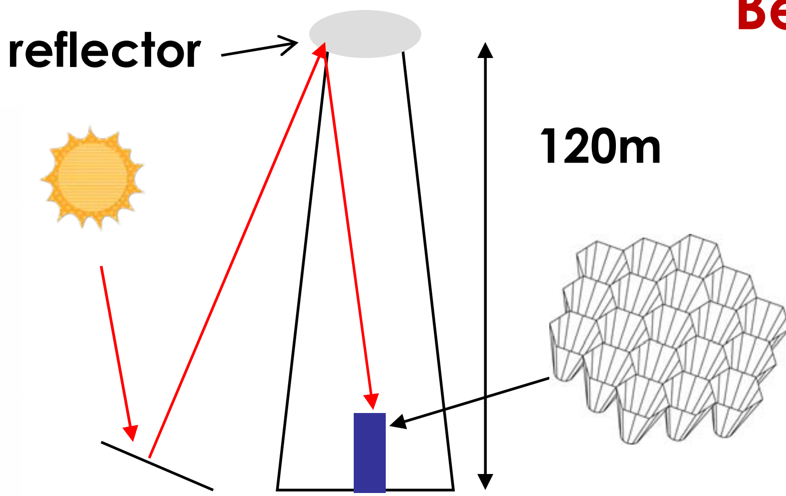
24 Hours: Hydrogen and Electricity generation

A solar plant has been established for the cadmium hydrogen cycle

- On ground reactor
- 100,000 kg H_2/day
- 10 towers 72MW



3842m² ~3% heliostat



Beam Down CSP

- 7 CPC
- d = 9.8m in, 3.6m out, 19m long

Parameter	High – Low	High – Low (H_2)
Heliostat	\$176 – 92 /m²	\$4.94 – \$4.02
Capacity	90 – 60 %	\$3.74 – \$5.53
Plant Capital	-25 – +25 %	\$4.77 – \$4.15

Base case 2015
\$4.46/kg H_2

Summary

Objective	Determine the feasibility and economics of a solar cadmium hydrogen cycle
Approach	Process steps experimental verification → Process concepts and flowsheet design → Solar plant design → Plant integration and H2A Analysis
Technical Accomplishments	➢ Established a CdO decomposer design concept ➢ Measured the Cd-O_2 vapor reaction rates ➢ Demonstrated an approach to using molten Cd to generate hydrogen ➢ Completed a preliminary solar cadmium hydrogen plant design
Future (FY09)	➢ Complete Cd vapor quench modeling studies

Future Work

CdO decomposition	➢ CdO decomposer prototype testing using a simulated solar source – fluidization and materials handling ➢ Decomposition of CdO from hydrolysis process
Cd vapor quenching	➢ Study the effect of quench rate on Cd-O_2 recombination ➢ Measure the molten cadmium – oxygen reaction rate
H_2 generation	➢ Conduct molten cadmium hydrolysis under pressure
Economics	➢ Closed system using helium as carrier gas - process flowsheet and economics studies