Solar Cadmium Hydrogen Production Cycle

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

Oxide Decomposition
CdO → Cd(g) + \( \frac{1}{2}O_2(g) \)
1450 C

Hydrogen Generation
Cd(l) + H_2O → CdO + H_2
450 C

Cadmium Vapor Quenching
Cd(g) → Cd(l)
1450 → 700 C

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

Cadmium Oxide Cycle
### Project 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

<table>
<thead>
<tr>
<th>Metric</th>
<th>Unit</th>
<th>2008</th>
<th>2012</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$ cost</td>
<td>$/kg H_2$</td>
<td>10.00</td>
<td>6.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Efficiency (LHV)</td>
<td>%</td>
<td>25</td>
<td>30</td>
<td>&gt;35</td>
</tr>
</tbody>
</table>
## Technical Approach

<table>
<thead>
<tr>
<th>CdO decomposition</th>
<th>➢ Determine the decomposition kinetics under various carrier gases</th>
</tr>
</thead>
</table>
| Cd vapor quenching | ➢ Measure the Cd-O₂ vapor reaction rate and determine the required quench rate  
➢ Determine via modeling if quenching is practical |
| H₂ 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

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Accomplishments</th>
<th>%Comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demonstrate CdO decomposition</td>
<td>➢ Effect of carrier gas on decomposition kinetics established</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>➢ Sub 1150°C decomposition demonstrated</td>
<td></td>
</tr>
<tr>
<td>Measure Cd-O$_2$ reaction rate</td>
<td>➢ Reaction rate wrt temperature and O$_2$ concentration measured</td>
<td>100</td>
</tr>
<tr>
<td>Demonstrate H$_2$ generation with Cd</td>
<td>➢ Demonstrated two pathways to use either molten or solid Cd to generate H$_2$</td>
<td>100</td>
</tr>
<tr>
<td>Modeling of Cd vapor quench</td>
<td>➢ Modeling studies of vapor quench on going</td>
<td>50</td>
</tr>
<tr>
<td>H2A Analysis</td>
<td>➢ Process flowsheet and solar field design completed</td>
<td>95</td>
</tr>
</tbody>
</table>
The CdO decomposition rate is a function of carrier gas and temperature.

The decomposition is controlled by the back reaction and oxygen diffusivity.

<table>
<thead>
<tr>
<th>Gas*</th>
<th>D ($10^4 m^2/s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.753</td>
</tr>
<tr>
<td>Ar</td>
<td>0.220</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.214</td>
</tr>
<tr>
<td>Air</td>
<td>0.153</td>
</tr>
</tbody>
</table>

*diffusivity of O₂ at room temp

The decomposition rate is shown as a function of temperature, with different carrier gases indicated. The data points show an increase in decomposition rate with temperature, influenced by the gas type.
CdO decomposition temperature was further reduced with slow heat rate.

The lower decomposition temperature will reduce solar field requirements.
Decomposition is very sensitive to O₂ diffusivity and back reaction

\[ \text{CdO(s)} \rightarrow \text{Cd(g)} + \frac{1}{2}\text{O}_2(\text{g}) \]

- Theoretical \( E_a \) is 241 kJ/mole
- Back reaction in O₂ rich environment leads to higher apparent \( E_a \)

\[
d\alpha/dt = k_o \cdot \exp(E_a/RT) \cdot (1-\alpha)^n
\]

Galwey & Brown

<table>
<thead>
<tr>
<th>Gas</th>
<th>( E_a ) (kJ/mole)</th>
<th>( k^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>248 ± 6</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>241 ± 10</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>268 ± 8</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>363 ± 10</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>384 ± 4</td>
<td></td>
</tr>
</tbody>
</table>

\( k^* = k_o \cdot \exp(E_a/RT_0) \)

- \( E_a \) is configuration independent
- \( k^* \) is strongly gas diffusion dependent

CdO Decomposition Data
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 O₂ flow through the furnace and react
- Gases are quenched after the reaction zone
- Reaction rate was calculated using:
  - O₂ reduction
  - Cd evap. Rate
  - Time of travel
A Mass Spec. measures the amount of O₂ 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)

$$\text{rate}_F = A_o \times \exp\left(\frac{E_a}{RT}\right) \times P_{O_2}^m P_{Cd}^n$$

$$\text{rate}_R = A_o \times \exp\left(\frac{E_a}{RT}\right) \times \left(\frac{1}{K_{eq}}\right) P_{O_2}^{m-1} P_{Cd}^{n-2}$$

$$\text{rate}_F = \text{rate}_R \text{ at equilibrium}$$

- Preliminary result give best fit with the experimental results at m = 0 and n=0.18
- Model implies Cd and O₂ 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 Generation w/ Molten Cd
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.

Hydrogen Generation w/ Molten Cd
Baseline flowsheet using air as carrier gas has been established (Efficiency 58% LHV)

**Solar Cd-H₂ Cycle Flowsheet**

**Baseline Flowsheet**

- **Air decomp. at 1450°C**
- **He decomp. at 1150°C**
- **Preheat**
- **Cd quench 1450→700°C**
- **He-O₂ separation**
- **Thermal storage (Cd at 700°C)**
- **Power generation**
- **Thermal storage (CdO at 450°C)**
- **Hydrogen generation w/molten Cd**
- **Steam-H₂ separation**

**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 H₂/day
- 10 towers 72MW

3842m² ~3% heliostat
reflector

Beam Down CSP

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

Parameter | High – Low | High – Low (H₂)
---|---|---
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 H₂

Solar Field Design and H₂ Cost
### Summary

<table>
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<th>Objective</th>
<th>Determine the feasibility and economics of a solar cadmium hydrogen cycle</th>
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<tbody>
<tr>
<td><strong>Approach</strong></td>
<td>Process steps experimental verification → Process concepts and flowsheet design → Solar plant design → Plant integration and H2A Analysis</td>
</tr>
</tbody>
</table>
| **Technical Accomplishments** | - Established a CdO decomposer design concept  
- Measured the Cd-O<sub>2</sub> 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

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
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</table>
| **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 |