Development of Solar Powered Thermochemical Production of Hydrogen from Water

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

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This presentation does not contain any proprietary, confidential, or otherwise restricted information
### 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

<table>
<thead>
<tr>
<th>Metric</th>
<th>Unit</th>
<th>2008 Target</th>
<th>2012 Target</th>
<th>2017 Target</th>
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</thead>
<tbody>
<tr>
<td>Solar Thermochemical Hydrogen Cost</td>
<td>$/kg H₂</td>
<td>10.00</td>
<td>6.00</td>
<td>3.00</td>
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<tr>
<td>Heliostat Capital Cost</td>
<td>$/m²</td>
<td>180</td>
<td>140</td>
<td>80</td>
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<tr>
<td>Process Energy Efficiency</td>
<td>%</td>
<td>25</td>
<td>30</td>
<td>&gt;35</td>
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</table>
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)
Cycle Feasibility Studies
Top Solar Thermochemical Cycles

**Volatile Metal Oxides**

- **Zinc oxide**
  \[ ZnO \xrightarrow{1600^\circ\text{C} - 1900^\circ\text{C}} Zn + \frac{1}{2}O_2 \]
  \[ Zn + H_2O \xrightarrow{300^\circ\text{C} - 400^\circ\text{C}} ZnO + H_2 \]

- **Cadmium Oxide**
  \[ CdO \xrightarrow{1450^\circ\text{C}} Cd + \frac{1}{2}O_2 \]
  \[ Cd + H_2O \xrightarrow{375^\circ\text{C} - 450^\circ\text{C}} CdO + H_2 \]

**Non-volatile Metal Oxides**

- **Sodium manganese**
  \[ Mn_2O_3 \xrightarrow{1500^\circ\text{C}} 2MnO + \frac{1}{2}O_2 \]
  \[ MnO + NaOH \xrightarrow{700^\circ\text{C}} NaMnO_2 + \frac{1}{2}H_2 \]
  \[ 2NaMnO_2 + H_2O \xrightarrow{350^\circ\text{C}} 2NaOH + Mn_2O_3 \]

- **Cobalt ferrite**
  \[ Co_{0.67}Fe_{2.33}O_4 \xrightarrow{1400^\circ\text{C}} Co_{0.67}Fe_{2.33}O_{4-d} + \frac{d}{2}O_2 \]
  \[ Co_{0.67}Fe_{2.33}O_{4-d} + dH_2O \xrightarrow{1000^\circ\text{C}} Co_{0.67}Fe_{2.33}O_4 + dH_2 \]

**Other**

- **Hybrid copper chloride**
  \[ Cu_2OCl_2 \rightarrow 2CuCl(l) + \frac{1}{2}O_2 \]
  \[ 2Cu + 2HCl(g) \rightarrow H_2(g) + 2CuCl(l) \]
  \[ 4CuCl \rightarrow 2Cu + 2CuCl_2 \]
  \[ 2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl \]

- **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$_2$O$_3$ results
- Extremely small product particles (>50 nm) give fast rates in H$_2$ generation step

- 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$_x$Fe$_{3-x}$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
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
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
The back reaction rate between Cd and O₂ was evaluated.

This information supports to design of a quench system to maximize Cd (and H₂) yields.

**Cadmium recombination rate**

<table>
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<tr>
<th>Temp (°C)</th>
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<th>2</th>
<th>1</th>
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<tr>
<td>1033</td>
<td>35.5**</td>
<td>44.5</td>
<td>47.4</td>
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<tr>
<td>1476</td>
<td>31.5</td>
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</tbody>
</table>

**cadmium-oxygen reaction rate (%/s)**

*O₂ flow rate (ml/min) total 150ml/min
Cu-Cl cycle & its advantages

- 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 CuCl₂-CuCl-HCl solutions, electrochemistry, risk analysis, etc.

The Hybrid Cu-Cl Cycle
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 H₂ for 2015 and $3.01/kg H₂ for 2025

• Initiated engineering lab-scale work
  – Test key steps in the conceptual design
  – First set of results very promising
Key hydrolysis reaction demonstrated: 
\[ \text{CuCl}_2 + \text{H}_2\text{O} = \text{Cu}_2\text{OCl}_2 + \text{HCl} \]

- Nebulizer reactor design concept successful
  - High heat and mass transfer zone
  - Very fine black powders of Cu\(_2\)OCl\(_2\) 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: Al₂O₃, SiC, and Haynes 214
- Design anticipated to yield improved efficiency for moderate to high temperatures (>1200 °C)

**Thermal Stress Plots**

**Tube Material Under Test**

**Prototype Reactor**
Solid Particle Receiver On-Sun Testing

- SPR evaluated on-sun at 2.5 MW\textsubscript{th} level
- Demonstrated Single pass \(\Delta T\) of \(\sim 200\) C
- Target \(\Delta T\) (SI-HyS) is between 300 – 500 C
- Materials evaluation underway

![SPR on the Power Tower](image)

**Typical Particle Heating Results**

- Mass rate = 8.55 kg/s
- DNI = 1000 W/m\^2
- Time = 0945
- Exit Temp = 189 C
- \(\Delta T = 174\) C

![Particle Curtain On-Sun](image)
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](image1)

![Pathlines showing internal currents](image2)
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 $\text{H}_2$ and $\text{O}_2$

Set of Counter-Rotating Rings

Reactive material
Insulation

$\text{H}_2\text{O}$
$\text{H}_2$, $\text{H}_2\text{O}$
$\text{O}_2$

Sandia National Laboratories
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

![Diagram of CR5 prototype construction with labels for various components such as injectors, housing, oxygen outlets, steam generator, and condensers.](image)
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.
## Current H2A Cost Estimates

### Comparison of current cost estimates:

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

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**
  – Feasibility 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