Aug 20th, 11:44 AM - 12:15 PM

Solar thermochemical hydrogen production project – progress toward industrial scale water splitting

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Solar Thermochemical Hydrogen Production Project – Progress Toward Industrial Scale Water Splitting

Presented by Roger Rennels
Solar ThermoChemical Hydrogen (STCH) Team

UNLV Renewable Energy Symposium
Las Vegas, NV
August 20th, 2008
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**
- University of Nevada, Las Vegas
- General Atomics
- Sandia National Laboratories
- University of Colorado, Boulder
- Argonne National Laboratory
- National Renewable Energy Laboratory
- TIAX, LLC
- ETH, Zurich

**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
Annual Direct Solar Radiation
Types of Concentrated Solar Collectors

- Trough System ~ 450°C
- Dish ~ 1200°C
- Power Tower ~ 1700°C
- Beam Down Tower ~ 1500°C
Trough System ~ 450°C
Dish ~ 1200°C
Power Tower ~ 1700°C
Beam Down Tower ~1500°C
The **RMS** has collected 395 cycles, encompassing 762 Reactions and more than 600 related literature citations *(updated 08/18/08)*

**URL:** http://shgr.unlv.edu
SHGR RMS – Search Engine

URL: http://shgr.unlv.edu
SHGR RMS – Web Portal Home Page

Analysis tools include:
- Automatic scoring system
- Cycle information search

URL: http://shgr.unlv.edu
Automatic cycle scoring system ranks potential thermochemical cycles based on:

- Solar collector type
- 15 pre-defined criteria
- Weighting factors

URL: http://shgr.unlv.edu
Project Objectives

Overall

• Select one or two cost competitive solar powered hydrogen production cycles for large scale demonstration
  • Perform experimental validations of the key components of prospective cycles
  • Develop solar receiver/reactor concepts
  • 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</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>
</tr>
</tbody>
</table>
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 (TIAAX)

**Task 5: Integration - Outreach**
- IEA collaboration (SNL)
- Heliostat R&D (SNL)
Cycle Feasibility Studies
Top Solar Thermochemical Cycles

**Volatile Metal Oxides**
- **Zinc oxide**
  \[ \text{ZnO} \xrightarrow{1600\,^\circ\text{C}-1900\,^\circ\text{C}} \text{Zn} + \frac{1}{2} \text{O}_2 \]
  \[ \text{Zn} + \text{H}_2\text{O} \xrightarrow{360\,^\circ\text{C}-400\,^\circ\text{C}} \text{ZnO} + \text{H}_2 \]
- **Cadmium Oxide**
  \[ \text{CdO} \xrightarrow{1450\,^\circ\text{C}} \text{Cd} + \frac{1}{2} \text{O}_2 \]
  \[ \text{Cd} + \text{H}_2\text{O} \xrightarrow{375-450\,^\circ\text{C}} \text{CdO} + \text{H}_2 \]

**Non-volatile Metal Oxides**
- **Sodium manganese**
  \[ \text{Mn}_2\text{O}_3 \xrightarrow{1500\,^\circ\text{C}} 2\text{MnO} + \frac{1}{2} \text{O}_2 \]
  \[ \text{MnO} + \text{NaOH} \xrightarrow{700\,^\circ\text{C}} \text{NaMnO}_2 + \frac{1}{2} \text{H}_2 \]
  \[ 2\text{NaMnO}_2 + \text{H}_2\text{O} \xrightarrow{350\,^\circ\text{C}} 2\text{NaOH} + \text{Mn}_2\text{O}_3 \]
- **Cobalt ferrite**
  \[ \text{Co}_{0.67}\text{Fe}_{2.33}\text{O}_4 \xrightarrow{1400\,^\circ\text{C}} \text{Co}_{0.67}\text{Fe}_{2.33}\text{O}_{4-\delta} + \frac{\delta}{2} \text{O}_2 \]
  \[ \text{Co}_{0.67}\text{Fe}_{2.33}\text{O}_{4-\delta} + \delta\text{H}_2\text{O} \xrightarrow{1000\,^\circ\text{C}} \text{Co}_{0.67}\text{Fe}_{2.33}\text{O}_4 + \delta\text{H}_2 \]
- **Other**
  - **Hybrid copper chloride**
    \[ \text{Cu}_2\text{OCl}_2 \rightarrow 2\text{CuCl}(l) + \frac{1}{2} \text{O}_2 \]
    \[ 2\text{Cu} + 2\text{HCl}(g) \rightarrow \text{H}_2(g) + 2\text{CuCl}(l) \]
    \[ 4\text{CuCl} \rightarrow 2\text{Cu} + 2\text{CuCl}_2 \]
    \[ 2\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl} \]

**Other**
- **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

Nano-size Zinc Conversion (<1 sec)
Aerosol processing can give fast rates for many high temperature cycles
Atomic Layer Deposition (ALD) of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$

- **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 $\text{O}_2$ evolved per mole ferrite affects cycle efficiency
- **ALD offers precise control of**
  - Stoichiometry
  - Film thickness
  - Specific surface area

![Iron oxide crystal structure](image)
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
Hydrogen Production via Cadmium Hydrolysis

The steam to hydrogen ratio was evaluated for Cd hydrolysis

The largest conversion is above the Cd melting point ~470°C
Evaluation of Cd – O₂ Back Reaction

The back reaction rate between Cd and O₂ was evaluated.

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

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>5*</th>
<th>2</th>
<th>1</th>
</tr>
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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>
<td></td>
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</tr>
</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.

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*The Hybrid Cu-Cl Cycle*
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 \( \text{Cu}_2\text{OCl}_2 \) 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: \( \text{Al}_2\text{O}_3 \), SiC, and Haynes 214
- Design anticipated to yield improved efficiency for moderate to high temperatures (>1200°C)

**Thermal Stress Plots**

**Prototype Reactor**
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 $\text{O}_2$

![Diagram of Counter-Rotating Rings](image)
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
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

Typical Particle Heating Results

SPR on the Power Tower

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
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.
### Current H2A Cost Estimates

#### Comparison of current cost estimates:

<table>
<thead>
<tr>
<th>Cycle</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>
</tr>
<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.
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
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
Imperative Goals

• *Downselect to 1-2 cycles*
  – This is planned for the end of FY08
• *Focus on materials development*
  – We are currently investigating materials development to support the solid particle receiver, the ferrite cycles, and the Mn/Zn cycles.
• *Heliostat cost reduction*
  – Heliostat costs must decrease from $180/m2 to $80/m2 in 2017
  – The research effort needed to support cost reductions is outlined in:
    • Heliostat Cost Reduction Study - SAND2007-3293
Critical Assumptions and Issues

- **Cost**
  - H2A is an accepted methodology used to assess each system based on common assumptions.

- **Parasitic system losses**
  - Process flowsheeting can be used as a starting point. Information from the feasibility studies is a required input.

- **High temperature materials operation**
  - Extreme environments degrade materials thermally and chemically. On-sun and lab scale testing are key to addressing this issue.
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 thermochemical hydrogen production is $0**
Selected Publications/Presentations


For further information

- Please contact Roger.Rennels@UNLV.edu.

“I believe that water will one day be employed as fuel, that hydrogen and oxygen constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable.”

Jules Verne,
The Mysterious Island (1874)