

II.I.1 Development of Solar-Powered Thermochemical Production of Hydrogen from Water*

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Objectives

- Quantify cycle thermodynamics, reactant/product equilibrium quantities for each cycle step, cycle step reaction kinetics for cost-effective thermochemical cycles.
- Optimize designs, processes and flow sheet performance to estimate minimum hydrogen cost for selected cycles.
- Develop cost-effective, high-temperature materials compatible with thermochemical processes.
- Demonstrate integrated pilot plant designs, including on-sun testing for up to three competitive cycles.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4.2.7) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (AU) High-Temperature Thermochemical Technology
- (AV) High-Temperature Robust Materials
- (AW) Concentrated Solar Energy Capital Cost
- (AX) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

TABLE 1. Solar-Driven High-Temperature Thermochemical Hydrogen Production

Characteristics	Units	2005 Target	2010 Target	2015 Target
Solar Thermochemical Hydrogen Cost	\$/gge H ₂	10	6	3
Solar Thermal Capital Installed Cost	\$/m ₂	200	170	130
Process Energy Efficiency	%	30	40	45

Process Energy Efficiency

All cycles being studied presently have estimated process thermal efficiencies higher than 30%. One process under investigation is estimated to provide process thermal efficiency of 59%.

Solar Thermal Capital Installed Cost

The primary contributor to solar thermal capital cost is in installed heliostats. The project is assessing current state of the technology to identify research and development to provide significant cost reduction in heliostat installed capital cost.

Solar Thermochemical Hydrogen Cost

Preliminary H2A estimates suggest that a hydrogen cost of \$3.90-4.90/gge from the hybrid sulfur cycle and \$4.60-\$6.85/gge from the zinc oxide cycle are achievable. Additional cycle research, and process and plant optimization are necessary and are being pursued

to establish confidence in these cost estimates and to identify opportunities for further cost reduction.

Accomplishments

Cycle database and scoring are completed:

- Approximately 353 unique cycles documented
- Analytical down-select to about 12 distinct cycles
- Three of these selected cycles are being investigated by the Nuclear Energy Program

Experimental work (kinetics, thermodynamics, materials and product characterization) underway for seven cycles:

- Zinc oxide
- Manganese oxide
- Cadmium carbonate
- Nickel manganese ferrite
- Zinc manganese ferrite
- Cobalt ferrite
- Hybrid copper chloride

Some system designs optimized for various operating temperatures and power requirements.

Computational fluid dynamics (CFD) modeling and simulation carried out to develop understanding of thermal transport in reactors and solid particle receivers.

analysis provides the theoretical chemical feasibility of individual cycle steps. An objective scoring process was developed and implemented to select the best, most cost-effective cycles for further study. Laboratory studies of reactant and product concentrations and reaction kinetics validate earlier theoretical predictions and provide necessary data for improved performance assessments and down-selection to a few cycles for demonstration, test and evaluation.

For hybrid cycles, electro-chemical cell designs are reviewed and modeled for ideal reactions, equilibrium reactions and for reactions incorporating process kinetics. Various electrolyte solutions are explored in the laboratory to optimize the electro-chemical process.

Chemical engineering system modeling software is applied to quantify thermal efficiency of conceptual flow charting of the most competitive thermo-chemical cycles, and plant design software is applied to provide capital cost estimates for the engineered thermo-chemical concept design. These systems studies provide the process thermal efficiency for later use in determining system efficiency as well as early estimates of cycle-specific hydrogen costs.

Solar thermal energy for high temperature processes ($T < 1,300^{\circ}\text{C}$) is being studied using a solid particle receiver (SPR) concept that accumulates directed solar energy from a field of heliostats. Solar thermal energy for ultra-high temperature processes ($T > 1,300^{\circ}\text{C}$) is being studied using cavity receiver concepts equipped with a secondary concentrator design. An engineering assessment of current heliostat cost and performance will define the benefits and R&D options to reduce significantly the costs of heliostat fields and associated towers that represent the primary cost drivers for a solar thermal energy processing system.

Capital and operating cost estimates developed from study products are used to identify the most attractive thermo-chemical cycles for test and evaluation in integrated closed-loop, bench-scale tests. Subsequent to successful integrated bench-scale, closed-loop demonstrations, earlier capital and operating costs will be refined and a “go/no-go” decision, based on economic potential, will be made whether or not to proceed to pilot plant design, and implementation planning.

Introduction

Hydrogen production by thermo-chemical water-splitting, a chemical process that accomplishes the decomposition of water into hydrogen and oxygen using only heat or a combination of heat and electrolysis instead of pure electrolysis, meets the goals for hydrogen production using only water and clean renewable solar energy. A comparative assessment has assessed 353 unique cycles and identified 12 potential thermochemical cycles grouped in about four chemical reaction classes for which additional reaction information is required. Detailed engineering analysis of the most competitive system concepts, using literature and laboratory data, will be applied to system design for testing and evaluation. A small-scale demonstration and a pilot plant design for the most competitive system concept will meet the project objective.

Approach

Thermo-chemical cycles were identified through literature search and contributions from cycle originators within and outside the project. Chemical reactions

Results

ZnO, Mn_2O_3 and Mixed Metal Oxides

Significant progress was made in the development of metal oxide and mixed metal oxide thermochemical water splitting cycles. Experiments and modeling were performed on the Zn/ZnO process, the MnO/ Mn_2O_3 process, mixed metal oxide and ferrite cycles, and for the

development of high temperature materials. Evaluation of the Zn/ZnO process included determination of ZnO decomposition kinetics, investigation of the ZnO dissociation process in aerosol flow, aerosol hydrolysis of Zn powder to produce hydrogen, and economic analyses of the overall process flowsheet. Thermogravimetric experiments were completed on ZnO dissociation, yielding an Arrhenius rate expression (Figure 1). The activation energy was estimated to be 353 ± 25.9 kJ/mol and the pre-exponential factor was $3.15 \times 10^6 \pm 5.54 \times 10^5$ s⁻¹. These model parameters conformed well to the L'vov mechanistic theory for subliming solids kinetics. Aerosol dissociation of ZnO was performed in a high temperature transport tube at temperatures between 1,600°C and 1,750°C (Figure 2). Conversion of ZnO to Zn in the hot zone of the reactor was as high as 80%, but recombination of Zn and oxygen during cooling and collection limited the Zn yield in the solid product to 26%. Aerosol hydrolysis of the zinc powder to close the cycle used a fluidized bed to co-feed zinc and steam, finding 25% conversions at temperatures below the melting point. These were with particles 1 micron in size; conversion is expected to increase with smaller

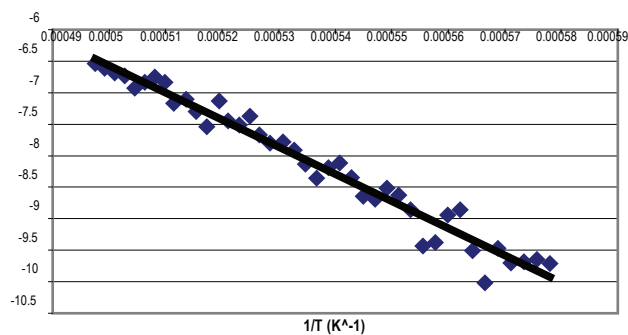


FIGURE 1. Arrhenius Analysis Shows Excellent Agreement with Kinetic Theory

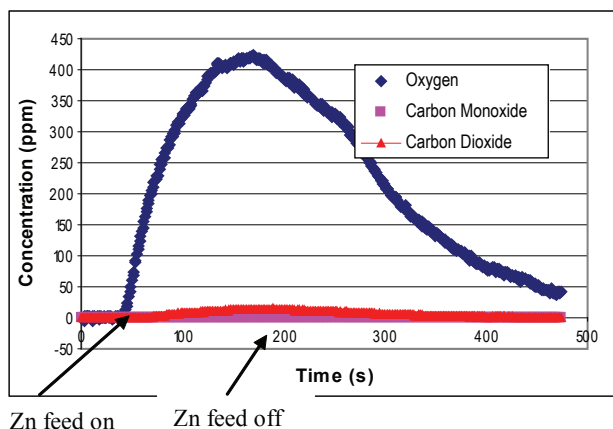


FIGURE 2. Experimental Dissociation of ZnO Aerosol

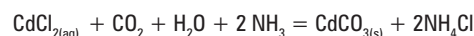
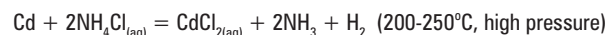
particles. Higher temperature routes to high conversion are also being investigated, with the goal of better diffusion of oxygen to unreacted zinc.

Two other thermochemical water splitting cycles are being studied. In the MnO/Mn₂O₃ cycle, reduction of Mn₂O₃ without melting or sintering was achieved at moderate temperatures (1400°C) and low vacuum. The reaction of MnO with NaOH has been achieved to full conversion at 700°C, and conditions for the cycle closing reaction were being studied. Synthesis of cobalt ferrite materials (CoFe₂O₄ and analogs) for mixed-metal oxides was successful using nitrate-salt precipitation, and synthetic routes using atomic layer deposition (ALD) are under development. The synthesized ferrites underwent partial reduction at 1,050°C in a thermal gravimetric analyzer (TGA).

Materials research has focused on the protection of high temperature materials (C/SiC) with ALD deposited refractory oxides (e.g., HfO₂). Deposition of hafnia on silicon carbide was completed successfully, but the 50 nm layer was either not robust enough or too thin to prevent oxidation in a solar environment. Nanolaminates of the oxides with more robust materials are currently under development.

Cadmium Carbonate

The literature showed a cadmium carbonate cycle, which was composed of two low temperature steps for hydrogen evolution:



NH₄Cl was eliminated to achieve a single step which operates at lower temperature and pressure:



The reaction has been demonstrated (0.27 moles, in 500 cc of solution, with some grinding), with reaction rates in the range of 1-5% of the Cd reacting per hour. The ammonium salt is used to dissolve any CdO barrier, thereby speeding the reaction. A temperature above about 100°C is necessary to partially decompose the ammonium bicarbonate to initiate the reaction. The product has been identified as CdCO₃ by x-ray diffraction. With a reaction rate of 5% per hour, one day solar production of cadmium can be reacted in less than 24 hours, thereby minimizing the cadmium inventory for a commercial solar plant working on a 24-hour inventory cycle time.

An Aspen flowsheet was developed for the cadmium carbonate cycle. The flowsheet showed a potential thermal efficiency of 68% (higher heating value, HHV)

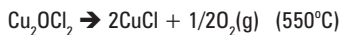
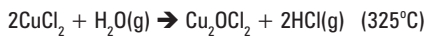
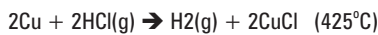
or 57% (lower heating value, LHV) that is much higher than any other cycle in the database.

Ferrites

Ferrite materials for ultra-high temperature hydrogen production continued under investigation. Currently, cobalt-ferrite (YSZ:Co_{0.67}Fe_{2.33}O₄) supported on yttria stabilized zirconia (YSZ) is yielding promising results in experimental trials. Samples were tested over several successive oxidation-reduction cycles with no decrease in hydrogen production or loss of structural integrity of the samples. The bulk of the testing of the ferrite materials has been done in conventional laboratory furnaces. On-sun testing was begun in June and hydrogen has been produced in tests using the baseline cobalt-ferrite material at the solar furnace facility at Sandia National Laboratories. Ferrite feasibility studies should be completed by the end of FY 2006. Figure 3 shows the test results after 31 cycles, demonstrating lattice durability and reasonably hydrogen generation after numerous cycles.

Hybrid Copper Chloride

Proof of principle has been demonstrated for all steps in the reaction:



This low temperature cycle is calculated to have promising efficiency (~40% LHV), but critical thermodynamic data must be determined experimentally. The enthalpy of formation of Cu₂OCl₂ at room temperature and its heat capacity as a function of temperature was measured:

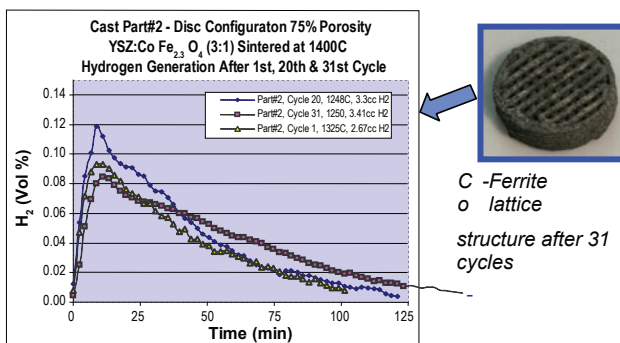


FIGURE 3. Cobalt-Ferrite Lattice Demonstrates Repeatable Hydrogen Generation

- The enthalpy of formation of solid Cu₂OCl₂ from the elements was measured as -381.3 kJ/mol at T = 298.15 K. This determination was based on calorimetric measurements of the enthalpies of solution of Cu₂OCl₂ (s), CuCl₂ (s), and CuO(s) in various HCl solutions.
- The heat capacity was measured over two temperature regions using adiabatic calorimetry (provided by Dr. Juliana Boerio-Goates of Brigham Young University) and differential scanning calorimetry. These results are compared with literature values as shown in Figure 4. Work is underway to reconcile differences in results from the two techniques and the literature.

Fabrication of batch and continuous electrochemical cells for the electrochemical reaction, 2CuCl → Cu + CuCl₂, is underway at both Argonne National Laboratory (ANL) and at the Gas Technology Institute (GTI). The cells at ANL are standard designs with some modifications to accommodate aggressive chemicals in the reaction. GTI cells will use GTI's proprietary anion exchange membrane.

Preliminary results from operation of the GTI cell are shown in Figures 5 and 6. The voltammogram results indicate that copper is produced beginning at about -0.57 V from 0.2 M CuCl solution (Figure 5). The copper precipitate is pictured in Figure 6. Scanning electron microscopy found that the precipitate particle size was in the range 5-50 micrometers. The GTI results suggest that carbon-based electrodes can produce micrometer particles and it is anticipated that nonometer particles can be produced with adjustment of reaction current and solution concentration.

Conclusions and Future Directions

Additional work is in progress in design and analysis of receiver and receiver reactor concepts as well as solar collector field studies, all in support of integrated

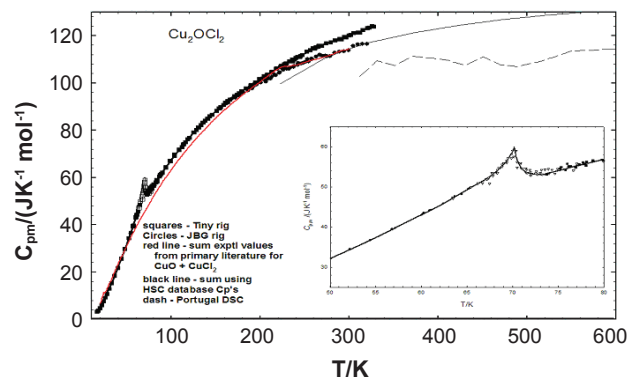


FIGURE 4. Heat Capacity Measurements for Cu₂OCl₂

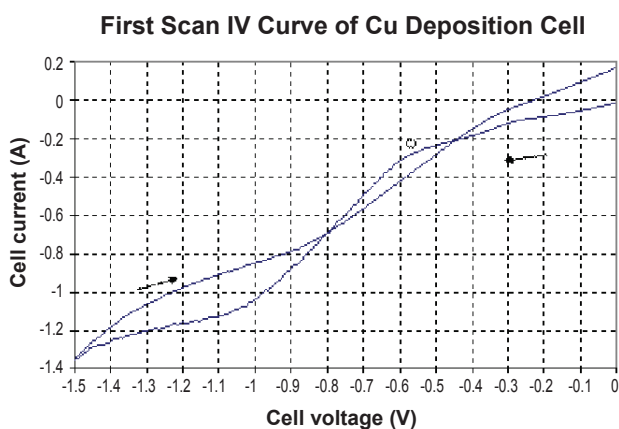


FIGURE 5. Voltammogram for the Electrochemical Reduction of CuCl_2



FIGURE 6. Zinc Powder Precipitate using the GTI Electrochemical Cell

systems analysis. These are still very much “works-in-progress” and will be reported later when the work reaches a more mature stage of development.

A number of promising thermochemical water-splitting cycles have been identified among the ~353 unique cycles identified. These are being subjected to quantitative study in the laboratory and theoretically to establish high-confidence data adequate to select the most competitive cycles for demonstration and pilot plant designs. Application of the H2A system costing tool, using necessarily preliminary data and assumptions has shown promise that solar-powered thermochemical water splitting can achieve intermediate cost goals in 2015 as described in the DOE Multi-Year Program Plan.

Work will continue in this project during the next and subsequent years. For the immediate future directions, the effort will:

- 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 the design of the solid particle receiver.

- Update H2A process economics.
- Investigate materials challenges for the very high temperature solar receiver and other system components.

Special Recognitions & Awards/Patents Issued

1. The ZnO cycle research was recognized with an award for excellence in research at the May 2005 Annual Program Review.

FY 2006 Publications/Presentations

1. Perkins, Chris, Paul Lichty, Allan Lewandowski, Carl Bingham, and Alan Weimer. “Reaction Kinetics of ZnO Decomposition for a Two-step Water Splitting Cycle.” SolarPACES 2006, Sevilla, Spain, June 23, 2006.
2. Francis, Todd, David M. King, Christopher Gump, and Alan Weimer. “Spinning Wheel Powder Feeding Device – Fundamentals and Applications,” AIChE Spring Meeting, Orlando, Florida, April 4, 2006.
3. Perkins, Chris and Alan Weimer. “Solar-Thermal Processing for Ultra-High Temperature Hydrogen Production,” Western States Energy Expo, Grand Junction, CO, February 24, 2006.
4. Weimer, Alan, and Chris Perkins. “Solar-thermal Processing for Ultra-high Temperature Chemistry,” University of Colorado Sustainable Energy Forum, Boulder, CO, February 7, 2006.
5. Perkins, Chris, Paul Lichty, and Alan Weimer. “Reaction Kinetics and Modeling of the Aerosol Thermal Decomposition of ZnO in for Solar Thermochemical Production of H_2 ,” AIChE Annual Meeting, Cincinnati, OH, November 1, 2005.
6. Perkins, Chris, Paul Lichty, Carl Bingham, and Alan Weimer. “Modeling and Optimization of Fluid-Wall Aerosol Reactors for Solar Thermochemical Hydrogen Production,” AIChE Annual Meeting, Cincinnati, OH. October 31, 2005.
7. Perkins, Chris, Jeremy Zartman, Hans Funke, Allan Lewandowski, and Alan Weimer. “Evaluation of the Solar Zn/ZnO Thermochemical Cycle for Sustainable Hydrogen Generation,” AIChE Annual Meeting, Cincinnati, OH. October 31, 2005.
8. Diver, R.B., Miller, J.E., Allendorf, M.D., Siegel, N.P., Hogan, R.E., “Solar Thermochemical Water-Splitting Ferrite-Cycle Heat Engines,” Proceedings of ISEC2006, Denver, CO, July 8-13, 2006.
9. Miller, J.E., Evans, L.R., Stuecker, J.N., Allendorf, M.D., Siegel, N.P., Diver, R.B., “Material Development for the CR5 Solar Thermochemical Heat Engine,” Proceedings of ISEC2006, Denver, CO, July 8-13, 2006.
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12. Kolb, G.J., Diver, R.B., Siegel, N.P., "Central-Station Solar Hydrogen Power Plant", ASME Journal of Solar Energy Engineering, In Press, 2006.
13. Chen, H, Chen, Y., Hsuan-Tsung Hsieh, H-T., Nathan Siegel, "CFD modeling of gas particle flow within a solid particle solar receiver," Proceedings of ISEC'06: American Solar Energy Society Solar 2006 Conference, July 8-13, 2006, Denver, CO, USA
14. Huajun Chen, Yitung Chen, Hsieh, H-T., Siegel, N., "CFD modeling of gas particle flow within a solid particle solar receiver," *ASME Journal of Solar Energy Engineering*, submitted.
15. Brown, L. C., "Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle," International Program for the Hydrogen Economy (IPHE) Solar Hydrogen Working Group, Seville, Spain, June 19-22, 2006.
16. Brown, L. C., "SHGR Cycle Evaluation Process," International Program for the Hydrogen Economy (IPHE) Solar Hydrogen Working Group, Seville, Spain, June 19-22, 2006.
17. Brown, L., "Solar Production of Hydrogen Using a Cadmium Based Thermochemical Cycle," American Institute of Chemical Engineers Spring Meeting, Orlando, FL, April 23-27, 2006.
18. Bunsen, Y Wong, Lloyd E. Brown, Gottfried E. Besenbruch, Yitung Chen, Richard Diver, B. Earl, Sean H. T. Hsieh, K. Kwan, Barry W. McQuillan, C. Perkins, P. Pohl, Roger Rennels, N. Siegel and, Alan Weimer, "Evaluation of Water-Splitting Thermochemical Hydrogen Cycles Applicable to Solar Thermal Systems," Solarpaces2006, Seville, Spain, June 20-23, 2006.
19. Barry W. McQuillan, Gottfried E. Besenbruch, Lloyd E. Brown, Roger A. Rennels and, Bunsen Y. Wong, "Metal Sulfate Water-Splitting Thermochemical Hydrogen Production Cycles," World Hydrogen Energy Congress, Lyon, France, June 13-16, 2006.