

II.F.1 Solar High-Temperature Water Splitting Cycle with Quantum Boost

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Subcontractors:

- ¹ Electrosynthesis Co. (ESC), Inc., Lancaster, NY
- ² Thermochemical Engineering Solutions (TCHEME), San Diego, CA
- ³ University of California, San Diego (UCSD), CA

Project Start Date: September 1, 2007

Project End Date: August 31, 2014

(W) Concentrated Solar Energy Capital Cost

(X) Coupling Concentrated Solar Energy and Thermochemical Cycles

Technical Targets

Table 1 presents the progress made, to date, in achieving the DOE technical targets as outlined in the §3.1.4 Multi-Year Research, Development and Demonstration Plan – Planned Program Activities for 2005-2017 (updated Oct. 2007 version), Table 3.1.9: Solar-Driven, Thermo-chemical High-Temperature Thermochemical Hydrogen Production.

TABLE 1. Progress towards Meeting Technical Targets for Solar-Driven High-Temperature Thermo-chemical Hydrogen Production^a

Characteristics	Units	U.S. DOE Targets			Project Status
		2008	2012	2017	
Solar-Driven High-Temperature Thermo-chemical Water Splitting Cycle Hydrogen Production Cost	\$/gasoline gallon equivalent H ₂	10.00	6.00	3.00	\$7.74 (2015) \$4.65 (2025)
Heliostat Capital Cost (installed cost)	\$/m ²	180	140	80	97 ^b
Process Energy Efficiency ^c	%	25	30	>35	19.3

^a Electrolytic system projected costs based on latest H2A analysis.

^b Based on SAIC glass-reinforced concrete structure with 10 sq.m. area and low production quantity.

^c Plant energy efficiency is defined as the energy of the hydrogen produced (lower heating value) divided by the sum of the energy delivered by the solar concentrator system plus any other net energy imports (electricity or heat) required for the process.

Fiscal Year (FY) 2011 Objectives

- Demonstrate a cost-effective high-temperature water splitting cycle for hydrogen production using concentrated solar energy.
- Evaluate photocatalytic and electrolytic options for generating hydrogen that meet DOE's solar high temperature H₂ production efficiency and cost goals.
- Confirm the feasibility of the selected cycle via bench-scale experiments.
- Determine the economic prospects of the selected cycle using the Aspen Plus chemical process model and H2A economic analysis program.
- Demonstrate a fully-integrated pilot-scale solar H₂ production unit.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials

FY 2011 Accomplishments

- An independent thermodynamic and chemical plant analysis reaffirmed that the cycle can be closed and indicated cycle viability.
- A high pressure reactor was developed to allow high temperature operation of the electrolytic cell. Various catalysts, cell configurations and membranes were tested.
- Steady progress was made and a total cell voltage of 0.8 V @ 160 mA/cm² and 1.02 V @ 300 mA/cm² (in short term runs) was attained while achieving near quantitative hydrogen production and sulfite conversion.
- Initial lab results prove the feasibility of the all-(liquid/gas) K₂SO₄/K₂S₂O₇ chemistry for the high-temperature oxygen evolution sub-cycle using potassium sulfate. Residual gas analysis equipment was added to the thermogravimetric analysis (TGA) unit at UCSD and the combined system is producing results.

- An improved Aspen Plus model of the sulfur-ammonia system was developed by UCSD and is being refined based on lab results and additional data.
- H2A economic model results were updated and aligned with DOE program assumptions showing the 2015 estimated hydrogen cost of \$7.74/kg and the 2025 cost of \$4.65/kg. The results assume no credit for excess electrical production. The process is being optimized to eliminate excess electrical production, improve efficiency and thus reduce cost.



Introduction

Thermo-chemical production of hydrogen by splitting water with solar energy is a sustainable and renewable method of producing hydrogen. However, the process must be proven to be efficient and cost effective if it is to compete with conventional energy sources.

Approach

To achieve the project objectives, the Bowman-Westinghouse “sulfur-family” hybrid thermo-chemical water splitting cycle (aka “Hybrid Sulfur, HyS” cycle) was modified by introducing ammonia as the working reagent, thus producing the sulfur-ammonia, or “SA,” cycle. The purpose of the modification is to attain a more efficient solar interface and less problematic chemical separation steps. Several versions of the SA cycle were developed and evaluated experimentally as well as analytically using the Aspen Plus chemical process simulator.

Two approaches were considered for the hydrogen production step of the SA cycle, namely: photocatalytic and electrolytic oxidation of ammonium sulfite to ammonium sulfate in an aqueous solution. Also, two sub-cycles have been considered for the oxygen evolution side of the SA cycle, namely: zinc sulfate/zinc oxide and potassium sulfate/potassium pyrosulfate sub-cycles. The laboratory testing and optimization of all the process steps for each version of the SA cycle were then carried out. Once the optimum configuration of the SA cycle has been identified and the cycle has been validated in closed loop operation in the lab, it will be scaled up and tested on-sun.

Results

Cycle Evaluation and Analysis

In previous years, significant work was performed on the photo-catalytic SA cycle. During the past year, work focused on the electrolytic SA cycle, which is summarized in the following equations:

$\text{SO}_{2(g)} + 2\text{NH}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow (\text{NH}_4)_2\text{SO}_{3(aq)}$	(1 – chem. absorption)	25°C
$(\text{NH}_4)_2\text{SO}_{3(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow (\text{NH}_4)_2\text{SO}_{4(aq)} + \text{H}_2$	(2 – electrolytic)	80-150°C
$(\text{NH}_4)_2\text{SO}_{4(aq)} + \text{K}_2\text{SO}_{4(l)} \rightarrow \text{K}_2\text{S}_2\text{O}_7(l) + 2\text{NH}_{3(g)} + \text{H}_2\text{O}_{(g)}$	(3 – solar thermal)	400°C
$\text{K}_2\text{S}_2\text{O}_7(l) \rightarrow \text{K}_2\text{SO}_{4(l)} + \text{SO}_{3(g)}$	(4 – solar thermal)	550°C
$\text{SO}_{3(g)} \rightarrow \text{SO}_{2(g)} + \frac{1}{2} \text{O}_{2(g)}$	(5 – solar thermal)	850°C

The electrolytic oxidation of the ammonium sulfite solution occurs more efficiently at higher temperatures requiring the development of a system capable of running at higher pressures. Reactions (3) and (4) form a sub-cycle by which potassium sulfate is reacted with ammonium sulfate in the low temperature reactor, to form potassium pyrosulfate. That substance is then fed to the medium temperature reactor where it is decomposed to SO_3 and K_2SO_4 again, closing the sub-cycle. The potassium sulfate and pyrosulfate form a miscible liquid melt that facilitates the separations and the movement of the chemicals in reactions (3) and (4). The oxygen production step (5) occurs at high temperature over a catalyst. Separation of the oxygen from SO_2 occurs when they are mixed with water in reaction (1). The net cycle reaction represented by reactions 1-5 is decomposition of water to form hydrogen and oxygen. All of the reaction steps described above have been demonstrated in the laboratory and shown to occur without undesirable side reactions. Figure 1 shows a schematic of the electrolytic SA cycle.

Independent Thermodynamic and Chemical Plant Analyses

An independent thermodynamic analysis of the feasibility of the SA Cycle was performed. The first step was to perform a preliminary thermodynamic analysis of the SA cycle. Subsequently a detailed analysis of the potassium pyrosulfate/electrolytic version of the SA cycle was performed. The analysis reaffirmed that the cycle can be closed and indicated cycle viability. The thermodynamic analysis was based on ideal solutions using HSC Chemistry 7.0 (Outotec Oyj, Espoo, Finland) augmented with SO_3 vapor pressure over $\text{K}_2\text{SO}_4/\text{K}_2\text{S}_2\text{O}_7$ solutions from reference [1]. The analysis was performed with Excel using add-in links to the HSC database enthalpy, and Gibbs energy functions. Vapor pressure data was fit using non-linear least squares analysis to generate functions for use in an Excel spreadsheet.

The major concerns to be addressed were in the oxygenation subsystem: the decomposition of ammonium sulfate, the formation of potassium pyrosulfate and the liberation of SO_3 from potassium pyrosulfate. Figure 2 shows details of the high temperature portions of the oxygen generation subsystem. The analysis assumed that the oxygen generation system would be operated at one bar and that the

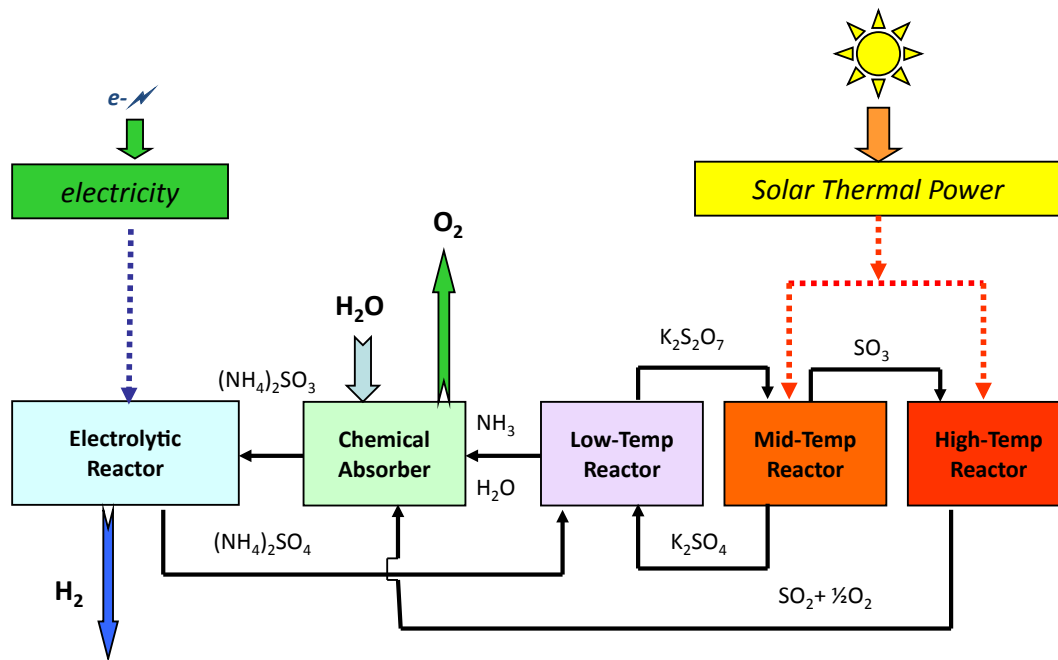


FIGURE 1. Schematic of the Electrolytic SA Cycle

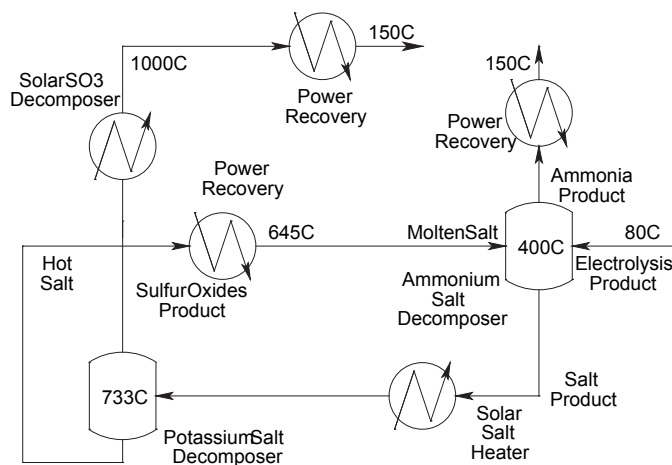


FIGURE 2. High-Temperature Portion of the SA Oxygen Generation Subsystem

ammonium sulfate decomposition step (low-temp reactor of Figure 1) would be accomplished at 400°C. For this analysis, the SO₃ decomposition temperature (high-temp reactor of Figure 1) was assumed to be 1,000°C. The composition of the electrolyte fed to the oxygen generation, obtained from ESC was H₂O:(NH₄)₂SO₄:(NH₄)₂SO₃ = 7.2:1:0.05. The minimum melting point of a K₂SO₄/K₂S₂O₇ mixture occurs at about 8.3 mole percent K₂SO₄ at about 400°C. The ratio K₂SO₄:K₂S₂O₇ = 2:10 in the molten salt fed to the ammonium salt decomposer was chosen such that, after absorbing one mole of SO₃ from the (NH₄)₂SO₄, the composition would be K₂SO₄:K₂S₂O₇ = 1:11, or 8.33 mole percent K₂SO₄.

The exact temperature of the NH₃/SO₃ separation is not of major importance, but it must be at least 400°C so that the K₂SO₄/K₂S₂O₇ product is molten. If slightly higher temperatures are required, there may be some recycle of SO₃ back to the electrolysis section with the NH₃ but this will have a minimal effect on the efficiency. What must be minimized is ammonium species accompanying the potassium salts into the high temperature section where the NH₃ will react in the catalytic SO₃ decomposer according to the reaction 2NH₃ + 3SO₃ → 3SO₂ + 3H₂O + N₂. If this occurs, not only will ammonia reduce the oxygen yield, and thus indirectly the amount of hydrogen generated, ammonia will have to be purchased continually or manufactured on site to make up the lost material.

The temperature of the potassium salt decomposer (the mid-temp reactor of Figure 1), 733°C is the temperature required to vaporize one mole of SO₃ from the salt product to return it to the required composition for feed to the ammonium salt decomposer. The stream must be cooled to 645°C such that when mixed with the electrolysis feed the resultant temperature of the ammonium salt decomposer is the specified 400°C. The only use of the heat from 733°C to 645°C is the production of electricity. This amount of heat is sufficient to power the electrolysis system at a voltage of 1.5 volts if the electricity is generated at 25% efficiency. If the hydrogen is produced at a reasonable voltage (0.5 to 0.8 volts) and the electricity is generated at normal efficiencies (30-40%) there will be a large excess production of electricity available for export. Since we intend to operate the hydrogen production system on a continuous 24/7 basis and the SO₃ decomposition system only during insolation, the hot molten salt will be available to generate electricity continuously.

Electro-Oxidation of Aqueous Ammonium Sulfite Solutions

Optimization of the electrolytic process continued at ESC. New catalysts and electrode materials have been screened at 80°C, with the most promising materials including spinels ($M_xN_{3-x}O_4$ where M,N=Fe/Ni/Co), platinum/cobalt mixtures and alternate felts. These materials were further screened in a new high pressure reactor which was built for this project and is shown in Figure 3. The high pressure reactor is capable of operation at 150 psi and 260°C. Cell performance with the Pt/Co catalyst at 130°C gave 0.8 V @ 160 mA/cm² and 1.02 V @ 300 mA/cm² as shown in Figure 4 with further improvements at higher temperature. Work also showed that the use of an undivided cell is most likely not possible at temperatures above 60°C, as the present cathode structure becomes inefficient with reduction of sulfite competing with hydrogen production.

High-Temperature Cycle Step Evaluation

Evaluation of the all-liquid/gas high-temperature cycle steps continued. As shown in Figure 5, TGA experiments were conducted to show the evolution of ammonia and water vapor at ~365°C, followed by evolution of sulfur trioxide at 496°C. A residual gas analyzer was used to detect the gases from the reaction. However, as tiny amounts (~10 mg) of reactants are used for the TGA with an argon



FIGURE 3. Pressure Vessels Required for Electrochemical Cell Operation at High Temperature

purge stream, the product concentrations are very diluted, and often not detectable. A large reactor system is being built to use ~10 g of reactants to study the reaction kinetics and evolution of gases products under more realistic operating conditions. The reactant ratios will be optimized to increase the temperature difference between the evolution of ammonia and SO₃.

Aspen Plus Process Analysis

The Florida Solar Energy Center (FSEC) supplied a copy of their model of the SA plant in Aspen Plus. Unfortunately, the data supplied was not sufficient to run the

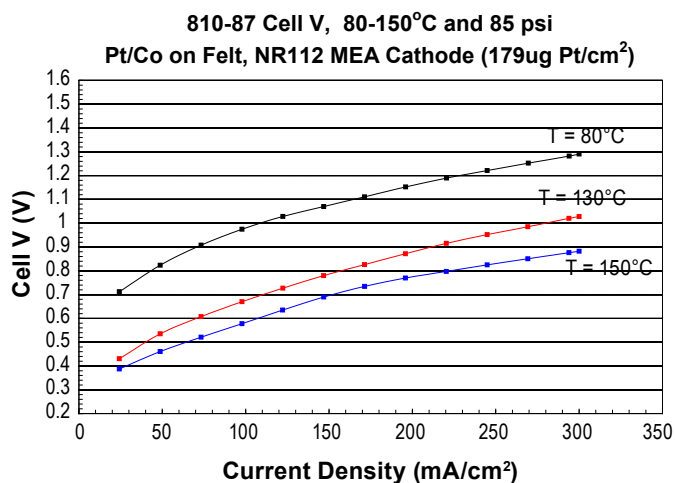


FIGURE 4. Cell Performance as a Function of Current Density and Temperature

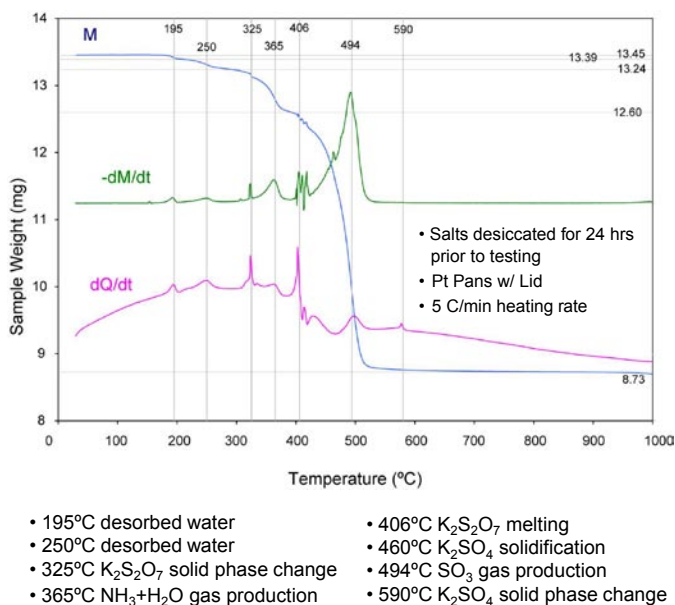


FIGURE 5. TGA/Differential Thermal Analysis of:
 $(NH_4)_2SO_4 + 2 K_2SO_4 + 8 K_2S_2O_7 \rightarrow 2 NH_3 + H_2O + 9 SO_3 + 10 K_2SO_4$

model with revised input values. UCSD supplied additional specifications for recycle streams within the plant so that the model could be run with new input values.

Using the FSEC model as a guide, UCSD is developing its own Aspen Plus model of the plant. This is being performed for several reasons. The first is to better understand all the characteristics of the plant model. Another reason is to include better thermodynamic data for some of the less common materials in the plant such as the molten sulfate/pyrosulfate mix in the oxygen section of the plant. To date, all units have been incorporated into the UCSD model and the material balance has been closed. Current work involves performing a process heat integration analysis, or pinch analysis, of the plant in order to place heat exchangers and optimize the thermal energy efficiency of the plant. UCSD is also developing rate/kinetic models of the individual unit operations in the plant.

Solar Field Optimization

The solar field configuration has continued to be updated as the thermo-chemical system evolves.

Evaluations were performed to determine the optimum way that the system could operate continuously on a 24/7 basis. The all-liquid $K_2SO_4/K_2S_2O_7$ system provides the opportunity to absorb and store heat directly in the reactants of the system. The molten salt solubility curves are such that a large excess of $K_2S_2O_7$ is needed to keep the mixture liquid, so much more heat capacity is present than is needed to operate the reactions. The sensible energy contained in the salts in the medium-temperature reactor is therefore also sufficient to provide the heat needed for the low-temperature reactor, and the excess energy is used to produce electricity that runs the electrolysis process. The highest-temperature oxygen evolution process can be operated in a solar-only mode using a separate high-temperature receiver, or electricity produced from the excess heat of the molten salt mixture can be used to operate that reaction 24/7 as well.

Economic Analysis

The H2A economic model for the electrolytic SA process was updated. Discrepancies between the inputs for the SA model and those of other groups were removed by using scaled values from the Sandia heliostat field analysis to update the solar field model. Updated results for the electrolytic process efficiency were also included in the calculation. The resulting estimated production costs for hydrogen were found to be \$7.74/kg in 2015, and \$4.65 in 2025.

The H2A cost analysis program was also used to examine the optimization of the electrolytic portion of the system. The electrolytic system design is a balance between capital costs for electrolytic cells and operating costs for electricity. Recent test data for the polarization curve of the electrolytic cell (i.e., voltage vs. current density) were combined with estimated costs from H2A for the electrolysis

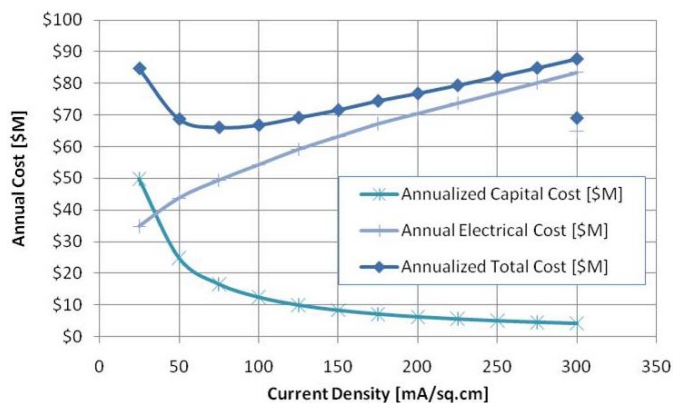


FIGURE 6. Economic Optimization Study Results

cells ($\$/m^2$) and for electricity. The capital costs were annualized using the capital recovery factor from H2A and combined with the annual electricity costs to obtain a levelized annual cost for the electrolytic system, and the calculation was repeated over a range of current densities from 25 mA/cm² to 300 mA/cm². The results are shown in Figure 6. At low current densities, the cost is high because of the large area of electrolysis cells needed to pass the required electrolysis current. At very high current density, the increase in cell overpotential leads to high electricity so the cost again increases. The lowest cost point is at 75 mA/cm². This is a much lower value than had been expected. For comparison, the target value of 0.8 V at 300 mA/cm² is plotted on the figure as the separate point to the far right – note that the minimum cost point predicted using our current data is actually lower than the cost for that set of conditions.

The conclusion from this study is that it is more important to focus our efforts on reducing cell voltage to reduce electrical costs rather than focusing on increasing current density to reduce capital costs. Sensitivity studies of the results confirm this conclusion. Increasing electricity costs drive the minimum cost to lower current densities, but not strongly. Doubling the cost of electricity reduces the minimum cost point from 75 to about 50 mA/cm². Likewise, doubling the capital cost of the electrolysis system components only moves the minimum cost point to about 100 mA/cm².

Conclusions and Future Directions

In summary:

- An independent thermodynamic and chemical plant analyses reaffirmed that the cycle can be closed and indicated cycle viability.
- Significant progress was made in reducing the cell voltage and increasing the current density of the electrolytic cell by operating at higher temperatures and with improved cell design. Improvements made over

the last year have enabled us to increase the current density by a factor of 2.5 times to 160 mA/cm² at a total cell voltage of 0.8 V.

- Additional evaluations of the all-liquid/gas high-temperature oxygen generation cycle steps continued to prove the subcycle feasibility.
- A new Aspen Plus chemical plant model has been developed that is more robust and more accurately models the thermodynamic characteristics of the model.
- Evaluations were performed that show the SA system with solar energy storage can operate continuously on a 24/7 basis.
- The H2A economic model for the electrolytic SA process was updated and aligned with the assumptions for other hydrogen production cycles. H2A analyses show that the lowest total annualized cost of hydrogen achieved to date at 0.6 V and 75 mA/cm² is actually lower than our target performance of 0.8 V and 300 mA/cm².

Activities planned for the upcoming year include:

- Further optimization of the electrolytic process and cell. This will include identification of catalysts that will reduce the over-potential at the anode and allow operation at high current densities. The best catalyst will be evaluated in longer term operation by performing a 500 hour durability test.
- Complete evaluation of the K₂SO₄ oxygen subcycle reactions. A large reactor system will be constructed to use ~10 g of reactants to study the reaction kinetics and evolution of gases products under more realistic operating conditions.
- Using Aspen Plus, optimize the thermal energy efficiency of the plant.
- Development of the thermal reactor/receiver designs including materials specification and testing.

- Development of the solar field configuration and design to match the final chemical plant requirements.
- Continue to update H2A economic analyses to document the potential cost of hydrogen from the SA cycle.

After completion of phase 1, the next phase of the project will involve laboratory validation of the closed-loop SA cycle leading to on-sun hydrogen production demonstration.

FY 2011 Publications/Presentations

1. Davenport, R., Taylor, R., Genders, D., Brown, L., Talbot, J., Presentation at the 2011 U.S. DOE Hydrogen and Fuel Cell Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 9–13, 2011. (PowerPoint presentation).
2. Wang, M., Ramzi, S., Talbot J., Thermogravimetric Study of a Solar Sulfur-Ammonia Thermochemical Water Splitting Cycle, Poster Presentation at the Jacobs School of Engineering Research Expo, University of California, San Diego, April 14, 2011.
3. Taylor, R., Genders, D., Davenport, R., Brown, L., Presentations at the STCH Technical Progress Meeting, University of Colorado, Boulder, October 27, 2010 (PowerPoint presentations).
4. Davenport, R., Taylor, R., T-Raissi, A., Genders, D., Muradov, N., Presentation at the DOE Annual Merit Review and Peer Evaluation Meeting – DOE Hydrogen Program and Vehicle Technologies Program, Washington D.C., June 8–11, 2010. (PowerPoint presentation).

References

1. Lindberg, D., Backman, R., & Chartrand, P. (2006). Thermodynamic evaluation and optimization of the (Na₂SO₄+K₂SO₄+Na₂S₂O₇+K₂S₂O₇) system. The Journal of Chemical Thermodynamics, 38(12), 1568-1583.