

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

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Subcontractors:

- Electrosynthesis Co., Inc., Lancaster, NY
- Thermochemical Engineering Solutions, San Diego, CA
- University of California, San Diego

Project Start Date: September 1, 2007

Project End Date: August 31, 2014

Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (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 2005-2015 (updated September 2011), 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 Thermochemical Hydrogen Production

Characteristics	Units	U.S. DOE Targets			Project Status
		2008	2012	2017	
Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost	\$/gge H ₂	10.00	6.00	3.00	\$7.74 ^a (2015) \$4.65 ^a (2025)
Heliostat Capital Cost (installed cost)	\$/m ²	180	140	80	97 ^b
Process Energy Efficiency ^c	%	25	30	>35	22.5% /41% ^d

gge – gasoline gallon equivalent

^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.

^d Plant energy efficiency without/with credit for excess electricity produced.

Fiscal Year (FY) 2012 Objectives

- Reduce the energy consumption of the electrolytic hydrogen production step by 20% by decreasing the voltage.
- Demonstrate the molten salt is liquid and will flow (low viscosity) so it is easily pumped.
- Demonstrate the NH₃ can be separated from the SO₃ by thermal decomposition thus avoiding potentially uneconomic gas separation processes.
- Develop a fully functioning and converging Aspen Plus[®] modeling of the Sulfur Ammonia (SA) cycle.
- Update the solar concentrating system to match the thermochemistry.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell

FY 2012 Accomplishments

- Improvements to electrocatalysts and high temperature operation have achieved cell voltages as low as 0.64 V at 50 mA/cm² and 0.85 V at 300 mA/cm².
- A 500 hour durability test was initiated to demonstrate the long-term stability of the electrolytic cell materials.
- Economic modeling initially showed that the minimum annualized cost was at current densities <100 mA/cm²; however, we may have to operate at higher current densities in order to minimize the effect of sulfite diffusing across the membrane.

- Lab results continue to prove the feasibility of the all-(liquid/gas) molten salt mixture of $(\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 4\text{K}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + 4\text{Na}_2\text{S}_2\text{O}_7$ chemistry for the high-temperature oxygen evolution sub-cycle.
- A thermochemical reactor and residual gas analysis equipment was used to show ammonia and sulfur trioxide can be evolved separately with a 25-50°C temperature difference.
- The melting points, densities and viscosities of the molten salt mixtures were measured; it was proven that the salts have low viscosities and can be easily pumped.
- The Aspen Plus® SA process modeling has been significantly improved and is now a robust fully functioning process tool.
- The Aspen Plus® model and the H2A economic model continued to be used to optimize and trade-off SA cycle configurations.
- A phase change storage approach was identified to allow 24/7 operation of the process, using NaCl, and will continue to be evaluated.



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 thermochemical 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

During the past year, work focused on the electrolytic SA cycle, which is summarized in the following equations:

- 1 Chemical Absorption: 25-50°C
 $\text{SO}_{2(\text{g})} + 2\text{NH}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow (\text{NH}_4)_2\text{SO}_{3(\text{aq})}$
- 2 Electrolytic: 80-150°C
 $(\text{NH}_4)_2\text{SO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow (\text{NH}_4)_2\text{SO}_{4(\text{aq})} + \text{H}_2$
- 3 Solar Thermal: 400-450°C
 $(\text{NH}_4)_2\text{SO}_{4(\text{aq})} + \text{K}_2\text{SO}_{4(\text{l})} \rightarrow \text{K}_2\text{S}_2\text{O}_{7(\text{l})} + 2\text{NH}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$
- 4 Solar Thermal: 550-850°C
 $\text{K}_2\text{S}_2\text{O}_{7(\text{l})} \rightarrow \text{K}_2\text{SO}_{4(\text{l})} + \text{SO}_{3(\text{g})}$
- 5 Solar Thermal: 850-1,000°C
 $\text{SO}_{3(\text{g})} \rightarrow \text{SO}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})}$

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. However, we are working to ensure that there are none in the electrolytic step and the SO_3 decomposition. Figure 1 shows a schematic of the electrolytic SA cycle.

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 ($\text{M}_x\text{N}_{3-x}\text{O}_4$ where $\text{M}, \text{N} = \text{Fe}/\text{Ni}/\text{Co}$), 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 2. Current potential curves were generated at 125°C for anolyte

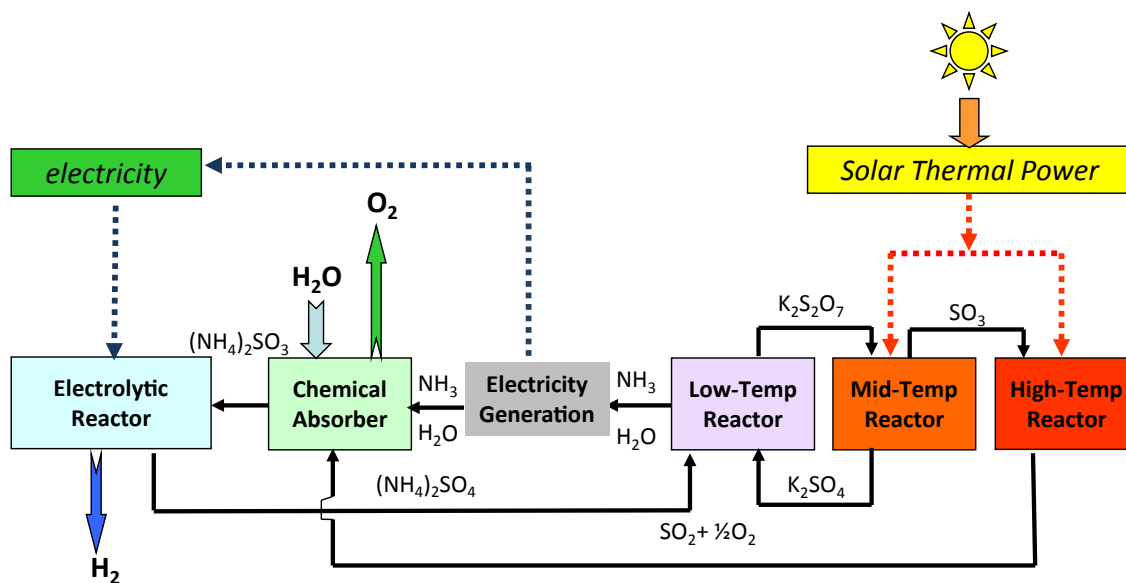


FIGURE 1. Schematic of the electrolytic SA cycle

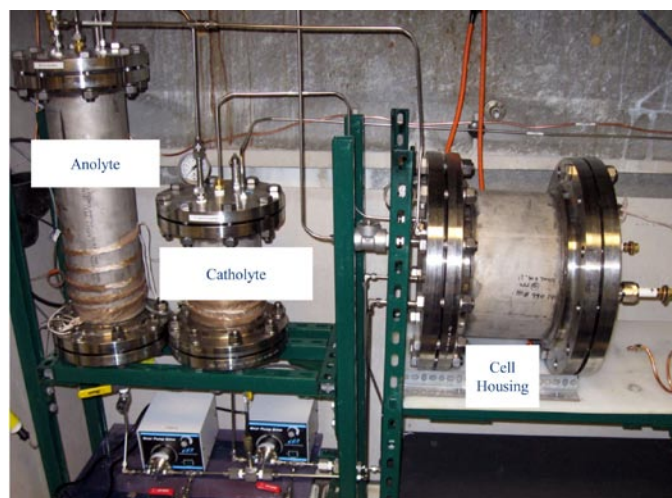


FIGURE 2. Pressure vessels required for electrochemical cell operation at high temperature

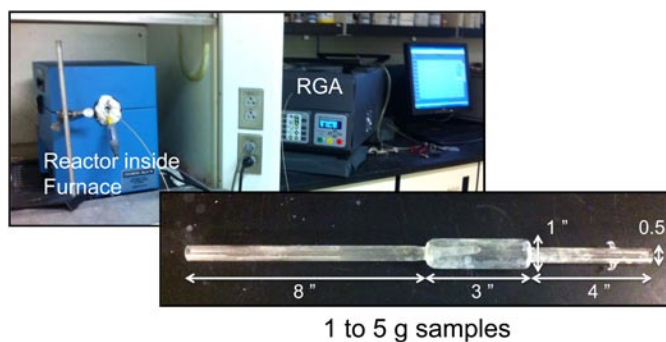


FIGURE 3. Thermochemical reactor system

compositions made up to simulate 0-90% conversions. These show that a voltage penalty of as low as 60 mV should be possible over this conversion range.

A 500-hour durability test was initiated at a current density of 50 mA/cm² and a temperature of 127°C. This ran for approximately 50 hours at which time it became apparent that the sulfite flux across the Nafion[®] membrane was too high. The resulting high concentration of sulfite on the cathode side of the cell resulted in reduced hydrogen current efficiencies. As a result of this testing, we have screened a number of alternate membrane materials and have identified a promising material that shows lower sulfite fluxes. Moreover we have shown that the high flux rates across the Nafion[®] -

type membranes occur after prolonged exposure to high temperature. The new membranes have been exposed to these same temperatures for up to three days and have maintained reasonable flux rates. Long-term testing will be initiated using these membranes.

High-Temperature Cycle Step Evaluation

Evaluation of the all-liquid/gas high-temperature cycle steps continued. A larger reactor system was built, as shown in Figure 3, to use up to ~10 g of reactants to study the evolution of gaseous products under more realistic operating conditions. A residual gas analyzer was used to detect the gases from the reaction. As shown in Figure 4, experiments were conducted to show the evolution of ammonia and water vapor at ~465°C, followed by evolution of sulfur trioxide at 500°C. The viscosity of the molten salt streams which would be entering and exiting the mid-temperature reactor was measured. The melting points and densities were also

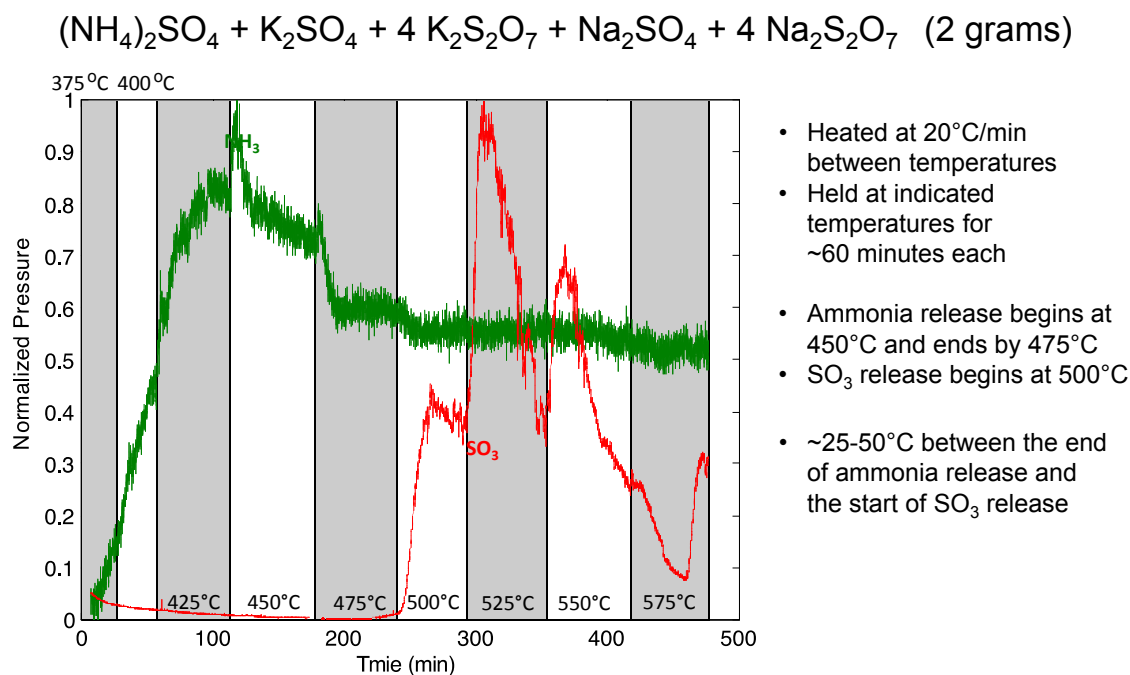


FIGURE 4. Residual gas analysis of oxygen generation half cycle

measured. It was determined that it should be easy to pump these molten salts with viscosities below ~8 cP as shown in Figure 5.

Aspen Plus® Process Analysis

UCSD developed a new Aspen Plus® model of the plant. A process heat integration analysis, or pinch analysis, of the plant was performed in order to place heat exchangers at optimal positions. Thermodynamic data from the literature were incorporated into the mid-temperature reactor, which decomposes molten pyrosulfates to sulfates and releases gaseous SO₃. Calculator blocks were utilized to obtain power requirements for the electrolyzer and the overall efficiency of the plant. Design specifications were placed in strategic areas of the model to aid convergence.

Energy from the solar-thermal heated reactors is recovered from the SO₂ + O₂ gas product of the high-temperature reactor and from the NH₃ + H₂O gas product of the low-temperature reactor. The gas product from the high-temperature reactor is used to preheat the SO₃ feed to the high-temperature reactor and the molten salt feed to the mid-temperature reactor. Energy recovery from the gas product of the low-temperature reactor is used to generate the electrical power for the electrolyzer, which produces the hydrogen product of the plant. The first option considered for this energy recovery is a single-flow condensing turbine that expands the NH₃ + H₂O vapor stream from 9 bar to a sub-atmospheric pressure maintained by a condenser. Another option is a standard Rankine steam power plant. The steam

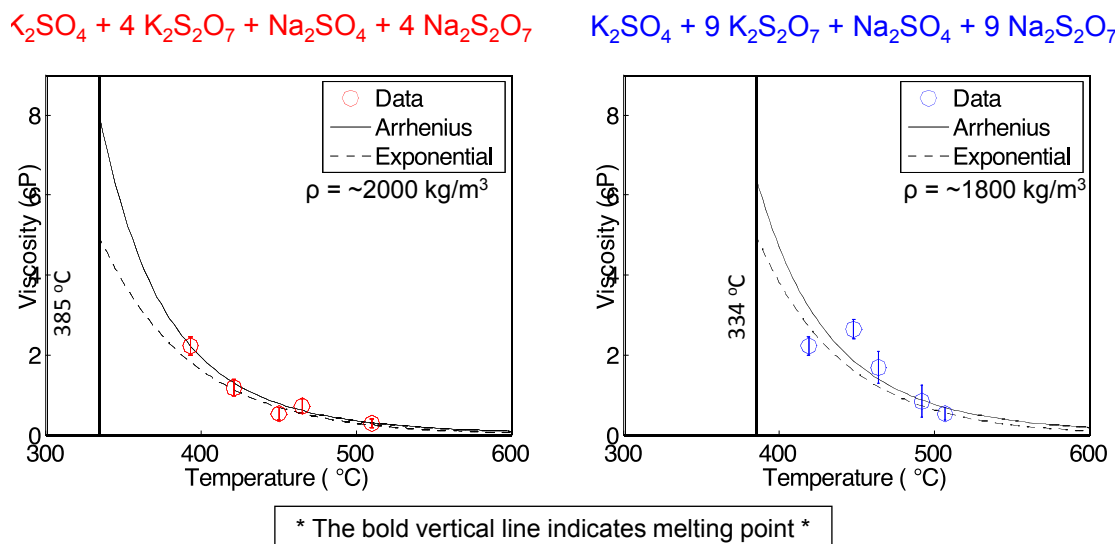
for this power plant would be produced by heat exchange from the NH₃ + H₂O vapor stream. Both options generate more power than needed for the electrolyzer. However, there are operational considerations that may make the steam power plant a preferred option. Further analysis of these trade-offs are required.

The total heat requirements of the solar reactors along with the total hydrogen product were exported to a calculator block that computes the overall efficiency of the plant. Currently, the overall process efficiency is 23%. The efficiency can be increased with further research into heat integration and different modes of power generation.

Process Flowsheet Alternatives

In addition to the process flowsheet from previous years, alternative configurations have been investigated using Aspen Plus®. The major alternatives are a different power recovery scheme and use of electricity to power the high temperature step, SO₃ decomposition.

The direct power recovery scheme proposed previously employs an expansion turbine in the ammonia vapor stream from the mid-temperature reactor. The alternative employs heat transfer from this same stream into a Rankine power plant. From an efficiency standpoint, there is little difference between the two schemes. The direct system has less heat exchange losses but the indirect scheme permits recovery of the heat of solution and heat of reaction from the recombination of SO₂ with aqueous ammonium hydroxide forming ammonium sulfite. Work will continue on both



- Viscosity of $\text{K}_2\text{SO}_4 + 4 \text{K}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + 4 \text{Na}_2\text{S}_2\text{O}_7$ ranged from 0.53 - 2.2 cP from 419 - 507 °C
- Viscosity of $\text{K}_2\text{SO}_4 + 9 \text{K}_2\text{S}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + 9 \text{Na}_2\text{S}_2\text{O}_7$ ranged from 0.29 - 2.3 cP from 393 - 510 °C
- We measured melting points, densities, and viscosities

FIGURE 5. Data showing molten salts can be easily pumped

schemes but the final selection between the two will be based on process economics. The direct scheme is much simpler but requires the power recovery to operate on a corrosive stream. Also, salt carryover into the ammonia stream must be rigorously avoided to prevent solids plate-out in the turbine.

The high-temperature step of the process uses less than 15% of the total thermal energy requirement. Since the process generates more electricity than required by the electrolysis step and since there is no credit given for export of excess electricity production, it made sense to consider electric heating to accomplish SO_3 decomposition. Use of an electrically heated decomposer (Joule Heating) may even make economic sense even if credit were given for export of excess electricity. The SO_3 reactor could be easily heated to above 1,500°C using silicon carbide heating elements thus increasing the conversion of SO_3 to SO_2 . The practical limit is about 1,200°C as above this temperature the reaction does not require catalysis so a quench would be required to retain the chemical conversion obtained at higher temperatures. The main advantages of Joule Heating are that solar costs would be reduced. Also, given a suitable thermal energy storage system, the complete chemical plant could operate continuously, independent of time of day or fluctuations in insolation due to passing clouds.

The cost of a solar installation is strongly dependent upon the highest temperature required. Not only are cavity radiation losses (proportional to T^4) lower, but the solar

field components are less expensive due to less stringent pointing accuracy requirements. Joule heating would remove the high temperature step from the top of a solar tower, increasing safety and reducing heat losses. Moreover, the reactor design would be considerably simplified. Instead of heating individual catalyst filled tubes or being forced to an atmospheric pressure decomposer design, a packed bed reactor could be designed with internal silicon carbide heating elements.

Probably the main advantage of using electric heat is that operation of the hydrogen plant would be completely decoupled, insofar as thermal energy storage allows, from diurnal and short-term fluctuations in solar insolation. Using the sodium chloride latent heat storage method described below, the chemical plant, both the electrolytic hydrogen generating system and the thermal oxygen generating system, can be operated around the clock under steady-state conditions.

Heat Storage

To allow the chemical plant to operate 24/7, storage of solar energy is needed. The most efficient form of storage is direct thermal storage. To provide the needs of the medium-temperature reactor, a maximum temperature of about 800°C is needed. SAIC has identified a unique phase change storage approach using molten NaCl that provides large amounts of

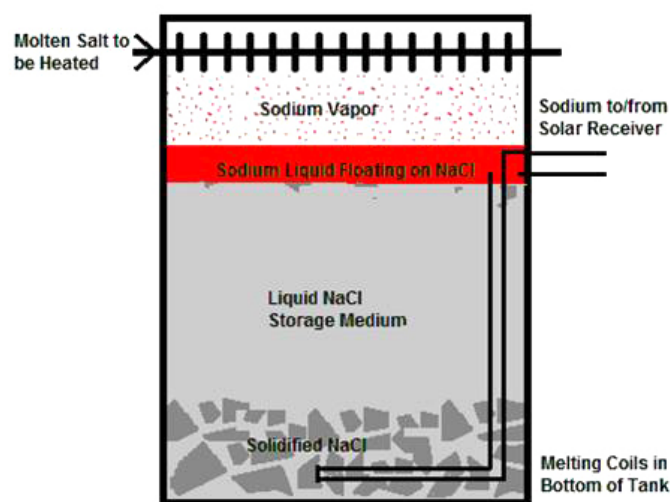


FIGURE 6. Schematic of a conceptual NaCl heat storage system

thermal capacity (481 kJ/kg) at this temperature, as well as providing an efficient means of extracting the heat from the storage to the molten salts. The storage consists of a stainless steel tank holding a volume of NaCl, with some head space above to accommodate the expansion/contraction of the salt as it changes phase. A schematic of the conceptual system is shown in Figure 6. A thin layer of liquid sodium metal (Na) floats on top of the molten NaCl and the head space is filled with Na vapor at its vapor pressure, which runs from about 0.5 to 1.5 bar over the temperature range expected. Pipes carrying the molten salt materials to be heated pass through the headspace in contact with the Na vapor, and the sodium acts as a heat pipe to transfer heat from the NaCl to the pipes. Solid NaCl that forms at the bottom of the Na pool sinks to the bottom (there is about a 30% reduction in volume upon solidification), so the Na remains in contact with liquid NaCl as the entire heat capacity of the storage is used. To re-melt the NaCl, pipes containing liquid sodium are placed at the bottom of the tank, and circulation from the solar receiver heats and re-melts the NaCl.

Solar Field Optimization

Further activity on the solar field configuration was delayed while waiting for the improvements to the Aspen Plus[®] model to be completed, so that it could be used for optimization of the heat interfaces to the solar field. These activities are ongoing.

Economic Analysis

H2A was used to evaluate the optimum operating conditions for the electrolytic portion of the system. The preliminary analysis evaluated the capital costs and electrical operating costs for the electrolysis process. Test data on the voltage versus current density was used. Using the H2A

defaults for the cost of the electrolytic cell and electricity, the conclusion was that the least-cost condition occurred at 50-75 mA/cm². Practical aspects of the electrolytic process, such as movement of sulfite through the membrane, may limit operating conditions to higher current densities. Also, we believe that the H2A capital cost values are low for the electrolytic cell, which would drive the optimum to higher current densities.

Conclusions and Future Directions

In summary:

- Improvements to electrocatalysts and high-temperature operation have improved the electrolytic cell performance. A 500-hour durability test was initiated but showed that extended operation at high temperature resulted in unacceptably high sulfite transfer rates. We have recently identified membranes that appear to have a significantly lower sulfite flux even after treatment at high temperature. The 500-hour durability test will be restarted to demonstrate long-term stability of this process.
- Lab results for the oxygen evolution sub-cycle using molten salt mixtures show ammonia and sulfur trioxide can be evolved separately with a 25-50°C temperature difference, thus avoiding difficult gas separation processes. The melting points, densities and viscosities of the molten salt mixtures were measured to prove that they have low viscosities and can be easily pumped.
- The Aspen Plus[®] SA process modeling was significantly improved and in conjunction with the H2A economic model, continue to be used to optimize and trade-off SA cycle configurations.
- Solar configuration evaluations were performed with the focus remaining on a central receiver system. A phase-change storage approach is being evaluated to allow 24/7 operation.

Activities planned for the upcoming year include:

- Continue with the electrolytic cell long-term (500 hour) test at higher current density and higher voltage. This would demonstrate the cathode stability in the presence of sulfite.
- Develop improved anode electrocatalysts that allow operation at low temperature while achieving low voltage.
- Continue evaluation of alternate membranes that can operate at high temperature with acceptable sulfite flux.
- Identify cathodes that preferentially evolve hydrogen in the presence of sulfite.
- Electrochemical cell design optimization and scale up.
- Develop a bench-scale, pressurized molten salt flow system to study rates of gas evolution.

- Continue refinement of the Aspen Plus® model to optimize the chemical process, including heating of the SO₃ reactor using electrical power.
- Evaluate NaCl phase change storage and its potential for supplying heat to the process on a 24/7 basis. Optimize the solar heliostat field configuration to supply the needed solar energy.
- Update the H2A analysis to include the optimized chemical plant configuration and solar field and storage configuration, and use H2A to identify the projected improvements possible due to advancing development in the various process and design areas.
- After completion of phase 1, the next phase of the project will involve bench-scale laboratory validation of the closed-loop SA cycle.

FY 2012 Publications/Presentations

1. Taylor, R., Genders, D., Brown, L., Talbot, J., Herz, R., Davenport, R., Presentation at the STCH Hydrogen Production Technology Team Review Meeting, La Jolla, California, July 10, 2012. (PowerPoint presentation).
2. Wang, M., “Study of the Thermochemistry for Oxygen Production for a Solar Sulfur-Ammonia Water-Splitting Process,” MS thesis, University of California, San Diego (2012).
3. Taylor, R., Davenport, R., Talbot, J., Genders, D., Brown, L., Herz, R., Overview and Status of the Sulfur Ammonia Thermochemical Hydrogen Production System for Splitting Water, Presentation at the 19th World Hydrogen Energy Conference 2012, Toronto, Ontario, Canada, June 3–7, 2012.
4. Taylor, R., Davenport, R., Solar Field Design and Integration for Thermochemical Hydrogen Production Systems, Poster presentation at the 19th World Hydrogen Energy Conference 2012, Toronto, Ontario, Canada, June 3–7, 2012.
5. Littlefield, J., Wang, M., Adoum, M., Talbot, J., Herz, R., Brown, L., Process Modeling and Thermochemical Experimental Analysis of the Solar Sulfur Ammonia Hydrogen Production Cycle, Presentation at the 19th World Hydrogen Energy Conference 2012, Toronto, Ontario, Canada, June 3–7, 2012.
6. Littlefield, J., Wang, M., Talbot, J., Herz, R., Brown, L., Process Modeling and Thermochemical Experimental Analysis of the Solar Sulfur Ammonia Hydrogen Production Cycle, submitted to *Energy Procedia* (2012).
7. Wang, M., Talbot, J., Herz, R., Brown, L., “Melting Point and Viscosity of Molten K₂SO₄ + K₂S₂O₇ + Na₂SO₄ + Na₂S₂O₇ Mixtures”, submitted to *Journal of Chemical and Engineering Data* (2012).
8. Genders, D., Symons, P., Brown, L., Electrochemical Oxidation of Ammonium Sulfite for the Sulfur Ammonia Thermochemical Hydrogen Production System, Poster presentation at the 19th World Hydrogen Energy Conference 2012, Toronto, Ontario, Canada, June 3–7, 2012.
9. Davenport, R., Taylor, R., Genders, D., Brown, L., Talbot, J., Presentation at the 2012 U.S. DOE Hydrogen and Fuel Cell Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 14–18, 2012. (PowerPoint presentation).
10. Littlefield, J., Herz, R., Brown, L., Solar Thermochemical Hydrogen Production Plant Design, Technical poster presented at the University of California, San Diego Jacobs School of Engineering Research Expo, La Jolla, California, April 12, 2012.
11. Taylor, R., Davenport, R., Woodard, K., Production of Hydrogen from Solar Energy, Technical paper and presentation at the 2011 World Energy Engineering Congress, Chicago, Illinois, October 13, 2011.
12. Taylor, R., Genders, D., Brown, L., Presentation at the STCH Technical Progress Meeting, Livermore, California, July 13, 2011. (PowerPoint presentation).
13. Luc, W., Woodard, K., Presentation at the SAIC and UCSD Team Internship Program (TIP) Presentations, Scaled Hydrogen Reactor Design and Electrode Catalyst Electrophoretic Deposition, Jacobs School of Engineering, UCSD, La Jolla, California, September 28, 2011. (PowerPoint presentation).