

IV.G.2 Sulfur-Iodine Thermochemical Cycle

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Start Date: September, 2002

Projected End Date: 2009 (completion of lab-scale experiments)

Objectives

- Evaluate the potential of the sulfur-iodine (S-I) thermochemical cycle for hydrogen production using nuclear energy
- Perform flowsheet analyses to evaluate S-I cycle process alternatives and cycle efficiency
- Design and construct lab scale experiments to demonstrate the three major process reactions of the S-I cycle
- Perform an integrated lab scale experiment to demonstrate closed-loop operation of the S-I cycle.
- Provide the technical basis for a 500 kW pilot scale experiment

Technical Barriers

This project addresses the following technical barriers of the Nuclear Hydrogen Initiative:

- High-temperature, corrosion resistant materials for extended service under thermochemical process conditions
- Process chemistry and thermodynamic data to support analysis of thermochemical cycle efficiency and operational characteristics
- Heat exchanger development for the high temperature reactor-process interface
- Hydrogen production facility costs

Approach

- Perform flowsheet analysis of S-I cycle process alternatives
- Construct experiments to investigate the major reactions of the S-I cycle using available materials and catalysts
- Perform stand-alone experiments to demonstrate chemistry and operation of the three major reactions for the S-I cycle
- Develop diagnostics and control strategies for stand-alone reaction sections
- Identify reactor-process interface heat exchange, safety, and system integration requirements
- Develop improved heat exchanger designs and materials for corrosive environment service
- Based on stand-alone reaction experiment results, design and construct integrated lab scale apparatus

- Perform integrated lab scale experiments to evaluate closed-loop operation
- Develop system designs, sizing, and materials for a 500 kWt pilot scale experiment

Accomplishments (through May 2005)

- Completed flowsheet analysis of alternate S-I cycle configurations and selected lab scale processes for the hydriodic acid (HI) and H₂SO₄ sections.
- Designed and constructed test apparatus for initial H₂SO₄ and HI section experiments.
- First series of H₂SO₄ decomposition tests at ambient pressure and 850°C completed.
- Initial series of HI reactive distillation tests completed (40 atm, 275°C).
- Extractive distillation apparatus has been constructed.
- Experiments on Bunsen reactor section and thermophysical property measurements on HI/I₂/H₂O vapor-liquid equilibrium initiated by Commissariat a l'Energie Atomique (CEA) through a DOE-CEA International Nuclear Energy Research Initiative (INERI) agreement.

Future Directions

FY2005

- Complete preparations and initial testing of the H₂SO₄ and HI extractive distillation sections.
- Complete acid decomposer ambient pressure tests and construct and perform high pressure tests for H₂SO₄ decomposition.
- Select HI distillation method for lab scale tests (extractive or reactive), construct HIx section major components from selected engineering materials.
- Complete Bunsen reactor construction at CEA.

FY2006

- Complete testing of H₂SO₄ and HI stand-alone sections in preparation for integrated lab scale experiments.

FY2007

- Complete facility and safety process preparations for the integrated lab scale experiment.
- Ship individual experiment sections to lab scale experiment site, assemble sections and necessary control and interface components, and initiate closed-loop testing.

FY2008

- Perform S-I hydrogen production test project in integrated lab-scale apparatus.
- Complete S-I pilot-scale experiment final design.

Introduction

Thermochemical cycle technology is one of the promising technologies being investigated by the Nuclear Hydrogen Initiative (NHI) for hydrogen production using nuclear energy. The NHI is focusing thermochemical cycle research efforts on the sulfur-based cycles (S-I and Hybrid Sulfur), to evaluate these cycles for hydrogen production using high temperature advanced reactors. This project describes work on the S-I cycle which is considered a leading candidate for hydrogen production from

nuclear power. The objective this work is to perform a lab scale demonstration of the S-I water splitting cycle to provide the technical basis for evaluation. The project will design, construct, and test the three major reaction sections that make up the S-I cycle. This project is being performed as part of the U.S.-DOE, French-CEA INERI agreement. The CEA is designing and testing the prime (Bunsen) reaction section. General Atomics is developing and testing the HI decomposition section. Sandia National Laboratories is developing and testing the H₂SO₄ decomposition section. These reaction sections are

being developed to initially function as stand-alone experiments, but will ultimately be assembled into an integrated lab scale experiment to perform a closed-loop demonstration of the S-I cycle. Key issues that must be addressed include high temperature materials in highly corrosive environments, process chemistry and thermophysical data uncertainties, innovative heat exchanger designs and materials to couple to the nuclear heat source, and systems evaluation of the potential performance and costs of these cycles for large scale hydrogen production.

Approach

Although a large number of thermochemical cycles were investigated in the 1970s, many were not viable and only a few were actually demonstrated. Most of these cycles were demonstrated in laboratory glassware and ambient pressure experiments. Due to the limited scope of previous work in this area, the NHI approach has undertaken a systematic research program to investigate these cycles, including evaluation of more recent membrane and materials advances and experimental work to examine processes in engineering materials and under conditions considered more representative of a large scale systems. The major task areas include flowsheet analyses to evaluate alternative configurations and basic data uncertainties, experimental studies to examine reaction chemistry and diagnostics for the S-I cycle, and evaluation of candidate materials for construction, catalysts, and membranes for the S-I cycle reactions. Based on the results of the initial analytic and experimental studies, NHI will then design, construct, and assemble the needed equipment for an integrated lab scale experiment to demonstrate closed-loop operation of the S-I cycle. Information for the operation of the integrated lab scale experiment will provide the technical basis for decisions on scaling to higher power levels at a pilot scale.

Results

Flowsheet analysis of S-I process options were completed in FY 2005 to support the design of process configurations for the lab scale experiment. Extractive distillation was selected as the HI distillation method. A direct contact heat exchange configuration was selected for the H_2SO_4 decomposition section and the CEA selected a

countercurrent reactor design for the Bunsen section. Experimental studies on the Bunsen section are now underway at the CEA. Diagnostics for this system have been validated and calibrated with pure vapor components. Measurements on the binary systems $\text{HI}/\text{H}_2\text{O}$, $\text{I}_2/\text{H}_2\text{O}$, and I_2/HI have also been performed, as well as preliminary total pressure measurements.

Reactive distillation experiments for the HI section have been conducted for both $\text{HI}/\text{H}_2\text{O}$ and $\text{HI}/\text{H}_2\text{O}/\text{I}_2$. Results show high levels of H_2 production with $\text{HI}/\text{H}_2\text{O}$ to demonstrate proof-of-concept for the process. However, when iodine is added to the solution, the driving force for the decomposition is reduced and hydrogen production is significantly reduced, as shown in Figure 1. The effect is relatively insensitive to the amount of iodine present. It is likely that the column is not efficiently separating the iodine from the HI and water before the reaction zone of the column. Based on the results of these experiments and cost and other technical uncertainties, extractive distillation was identified as the method for further development and demonstration. Construction of the extractive distillation apparatus has been completed and initial experiments are underway.

Sulfuric acid decomposition experiments have been completed under ambient pressure conditions at temperature up to 850°C . The construction of the sulfuric acid apparatus is modular to allow testing of a range of boiler, superheater, and decomposer designs. The apparatus is constructed of alloys that could potentially be used in a larger scale system. The apparatus consists of two sections that are

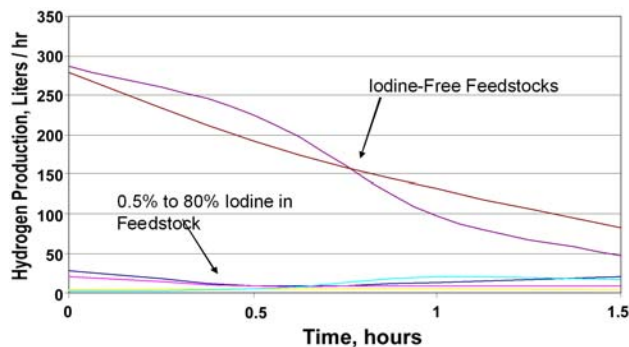


Figure 1. Hydrogen Production in Reactive Distillation Experiments with and without Iodine in the Feedstock

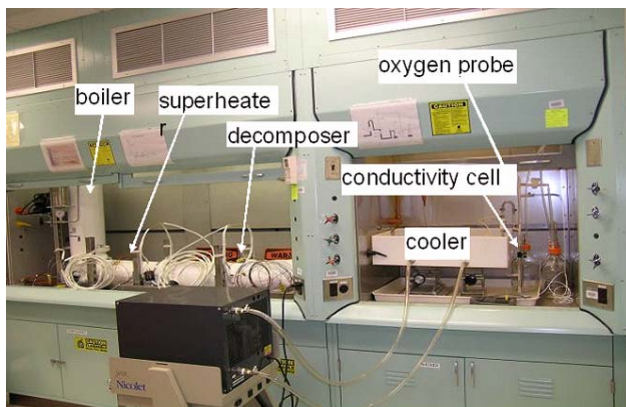


Figure 2. Ambient Pressure Sulfuric Acid Boiler, Superheater, Decomposer Apparatus

contained in adjacent fume hoods, as shown in Figure 2. Concentrated liquid acid is pumped into the top of the boiler where the acid vaporizes as it flows downward through a column of acid-resistant ceramic pellets at 650°C to decompose the acid to SO_3 and H_2O . This stream then passes through a catalyst-packed decomposer where the SO_3 decomposes to SO_2 and 0.5 O_2 . The initial catalyst is 1 wt% platinum on zirconia pellets. Ambient pressure results show significant corrosion on metal surfaces with two-phase acid contact, and designs to mitigate these effects are being developed. Fourier Transform Infrared (FTIR) spectroscopy procedures are being developed to provide in-situ H_2O , SO_2 , and SO_3 concentration data.

Conclusions

- The results of the HI distillation experiments show that high levels of hydrogen production can be achieved at temperatures of 275°C with current catalysts.
- Iodine in the mixture significantly inhibits the decomposition of HI, leading to the selection of extractive distillation as the recommended HI distillation method.
- Sulfuric acid decomposition tests have confirmed analytic estimates of SO_2 generation at 850°C and ambient pressure.
- Significant corrosion was observed in boiling and condensing regions, indicating the need for innovative heat exchanger designs and ceramic components.

- A direct contact heat exchange flowsheet has been selected as the recommended sulfuric acid decomposition section approach.

Publications

1. Bunsen Wong, et.al., "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE Spring Meeting, April 2005, Atlanta
2. Benjamin E. Russ, et.al., "HI Decomposition- A Comparison of Reactive and Extractive Distillation Techniques for the Sulfur-Iodine Process," AIChE Spring Meeting, April 2005, Atlanta
3. Paul M. Mathias, Lloyd C. Brown, "Quantitative Analysis of the Sulfur-Iodine Cycle Through Process Simulation," AIChE Spring Meeting, April 2005, Atlanta
4. Paul M. Mathias, Lloyd C. Brown, "Phase Equilibria and Thermodynamic Properties of the Sulfur-Iodine Cycle," AIChE Spring Meeting, April 2005, Atlanta
5. Bunsen Wong, et.al., "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE Spring Meeting, April 2005, Atlanta
6. "Metallurgical and Corrosion Characterization of Structural Materials for the National Hydrogen Initiative", Ajit Roy, Radhakrishnan Santhanakrishnan, Ancila Kaiparambil, Bunsen Wong, Gottfried Besenbruch, Lloyd Brown Materials Science & Technology 2005, Symposium: Materials for the Hydrogen Economy, Sep. 25-28, 2005, Pittsburgh, PA
7. Fred Gelbard and Paul Pickard, "Lab-Scale Catalytic Decomposition of Sulfuric Acid with Scalable Materials," AIChE Spring Meeting, April 2005, Atlanta
8. Dion Rivera and M. Kathleen Alam, "In Situ Monitoring of Sulfuric Acid decomposition by Fourier Transform Infrared (FT-IR) Spectroscopy in the Sulfur Iodine Thermochemical Reaction for the Production of Hydrogen," Pittcon Analytical Conference, Feb. 28 - Mar. 4 2005, Orlando, Florida

Other Reports

1. Bunsen Wong, Lloyd C. Brown, Robert Buckingham, Gottfried Besenbruch, Gary Polansky, and Paul Pickard, "Engineering Materials Requirements Assessment for the SI Thermochemical Cycle," GA-A24902/SAND2004-681, February 2005.

2. Lloyd Brown, Bob Buckingham, Ben Russ, Gottfried Besenbruch, Fred Gelbard, Paul Pickard, Jean-Marc Borgard, "Design of the Integrated Lab-Scale Experiment for the Sulfur-Iodine Thermochemical Cycle," INERI Report, September 30, 2004

Presentations

1. Numerous presentations on the S-I project have been given by project participants including:
2. NHI Semiannual Review Meetings (September 2004, March 2005)
3. US French INERI Review Meetings (US, October 2004, France, April 2005)
4. Overview presentations for the Nuclear Energy Research Advisory Committee (NERAC), and the NRC Advisory Committee on Reactor Safeguards (ACRS)
5. University Consortium Quarterly Reviews (UNLVRF High Temperature Heat Exchanger Program)