

II.G.2 Sulfur-Iodine Thermochemical Cycle

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Start Date: September 2002
Projected End Date: 2008 (completion of lab
scale experiments)

- 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 requirements, system integration and control strategies
- Develop improved materials and heat exchanger designs for high temperature corrosive environment service
- 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 kWth pilot scale experiment

Objectives

- Evaluate the potential of the Sulfur-Iodine (S-I) thermochemical cycle for hydrogen production using nuclear energy
- Perform an integrated lab-scale experiment to demonstrate closed-loop operation of the S-I cycle
- Provide the technical basis for scale-up decisions on 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 reactor-process interface
- Hydrogen production facility costs

Approach

- Perform flowsheet analysis of S-I cycle process alternatives

Accomplishments (through May 2006)

- Designed and constructed test apparatus for H_2SO_4 decomposition up to 875°C and 11 bar pressure, and developed and tested first direct contact heat exchanger experiments
- Developed new fully integrated high temperature acid vaporized decomposer-recuperator based on corrosion resistant SiC and glass lined steel materials
- Reactive distillation for hydrogen iodide (HI) decomposition tests completed (40 atm, 275°C).
- Extractive distillation experiments performed to quantify required H_3PO_4 concentrations
- Bunsen reactor section constructed and separate Bunsen reactor section experiments have been performed through DOE-Commissariat a Energie Atomique (CEA) International Nuclear Energy Research Initiative (INERI) agreement

Future Directions

FY 2007

- Complete testing of H_2SO_4 decomposition and HI extractive distillation and decomposition sections
- Complete Bunsen section testing (CEA)
- Complete facility and safety process preparations for the integrated lab-scale experiment

- Ship and assemble the three reaction sections to the General Atomics test site and perform initial shakedown testing
- Perform system integration tests to assess process performance, controls, and section interactions

FY 2008

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

Introduction

Thermochemical cycles are one of the promising technologies being investigated by the Nuclear Hydrogen Initiative (NHI) for hydrogen production using nuclear energy. The NHI is investigating the sulfur-based thermochemical cycles (Sulfur-Iodine and Hybrid Sulfur) to evaluate the potential of these cycles for use in hydrogen production using high temperature advanced reactors. This project focuses on the S-I cycle with the objective of developing an integrated lab-scale experiment to provide the technical basis for scale-up decisions. This project is being performed as part of the US-DOE, French-CEA International Nuclear Energy Research Initiative (INERI) agreement. The CEA is designing and testing the primary (Bunsen) reaction section. General Atomics (GA) is developing and testing the HI decomposition section. Sandia National Laboratories (SNL) is developing and testing the H₂SO₄ decomposition section. These three reaction sections are being developed initially as stand-alone experiments, but with the intent to ultimately assemble the three sections 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

The approach taken in this project has been to first investigate process configuration in flowsheet analyses to determine the most promising approaches, and then conduct experimental studies to provide data on reaction chemistry, and the performance of materials of construction and catalysts. Supporting studies on construction material corrosion, catalyst stability, and separation membranes are also being pursued as part of

the NHI. The S-I reaction sections are being designed and tested by the three organizations (SNL, GA, French CEA) to provide the technology and experimental hardware for the integrated lab-scale experiment to demonstrate closed-loop operation. Information from the integrated lab-scale experiment will provide the technical basis for decisions on scaling to higher power levels at a pilot scale.

Results

Based on the flowsheet analyses performed in FY 2005 to evaluate cycle configurations options, experiments have been performed to evaluate extractive distillation approach for the HI decomposition section and two alternative approaches for H₂SO₄ decomposition. These experimental studies will provide the data and experience base for the construction of the integrated laboratory scale experiment section in FY 2007.

Sulfuric Acid Decomposition Section: Sulfuric acid decomposition experiments have been completed at temperatures up to 900°C using two different experiment approaches. The first series of decomposition tests used an apparatus based on superalloys for the high temperature sections. Engineering approaches were developed to minimize corrosion, and acid decomposition experiments were successfully conducted up to 875°C and 11 bar. Recent experimental work has focused on a more robust and integrated configuration based on ceramic materials (SiC) in the high temperature regions, and glass- or Teflon-lined steel in low temperature areas. The new configuration uses a bayonet heat exchanger using SiC components as an integrated vaporizer, superheater, and decomposer. This new design was developed and tested to both minimize corrosion issues and simplify components and connections in these high temperature environments. The bayonet apparatus is also far more compact and robust to variations operating conditions.

The metallic apparatus was configured with a boiler, catalytic decomposer and a direct contact heat exchanger (DCHX) to recover unreacted acid and recuperate heat from the high temperature output stream. The apparatus is shown in Figure 1. Concentrated liquid acid enters the DCHX where it is heated from the rising decomposer vapor effluent. Unreacted acid is also condensed into the falling liquid acid stream. The liquid acid from the DCHX then is vaporized and decomposed to form SO₃ and H₂O and then catalytically decomposed at nominally 850°C to form SO₂. These tests were the first to demonstrate DCHX operation with minimal corrosion.

Subsequent experiments have focused on the new SiC bayonet design to minimize corrosion concerns and provide a more compact and robust system. In

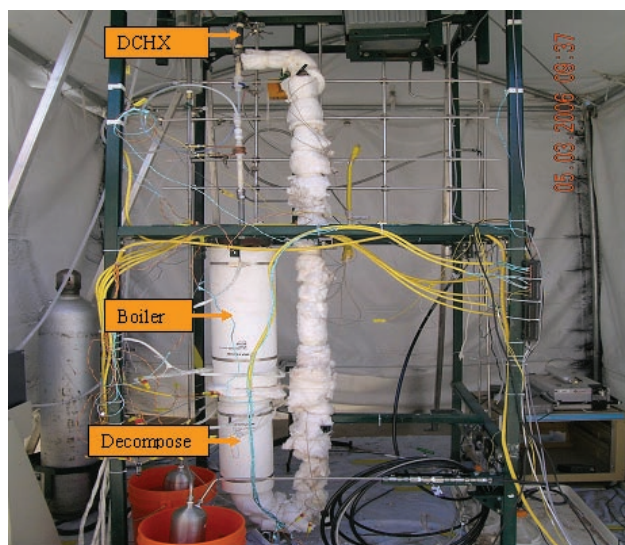


FIGURE 1. Metallic Boiler and Decomposer with Ceramic Direct Contact Heat Exchanger

the bayonet design the acid boiler and decomposer are incorporated into a single SiC-based unit which also provides heat recuperation between the reactor effluent and incoming liquid acid stream. Four acid tests have been performed and heat recovery from the effluent stream was excellent and the acid conversion fraction was approximately 65% at 850°C under ambient pressure.

HI Decomposition Section: The development of the HI decomposition section is based on an extractive distillation approach which allows I_2 be separated from the blend of hydrogen iodide, iodine, and water (HIx) feed stream before decomposition. Experiments during the past year have focused on the liquid-liquid extraction step where the H_3PO_4 strips the HI and water from the HIx feed solution. The two factors investigated are the H_3PO_4 concentration and the H_3PO_4 :HIx flow ratio. Figure 2 illustrates the trends for these effects. There is an improvement in the HI extraction from the HIx feed solution as the H_3PO_4 concentration increases from ~90 to 98 wt% for the 1:1 flow ratio. However, for the 3:1 flow ratio runs, the improvement from the increasing H_3PO_4 concentration reaches a maximum around 94 wt% acid for these test conditions. This suggests there may be an optimum set of conditions for the extraction column, balancing the energy cost of concentrating the phosphoric acid with the cost of pumping larger volumes of acid. Additional studies of the thermodynamics of the extraction chemistry are planned.

Conclusions

The results of the HI distillation experiments show that high levels of hydrogen production can be

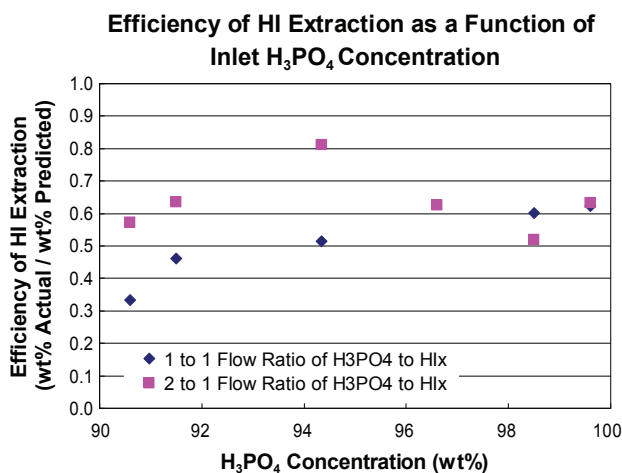


FIGURE 2. Effect of H_3PO_4 Concentration on HI Extraction

achieved at temperatures of 275°C with current catalysts. Since iodine in the mixture significantly inhibits the decomposition of HI, current experiments are focusing on extractive distillation as the HI distillation method. Current experiments are being conducted to identify the optimum H_3PO_4 concentrations for the extractive distillation approach. The H_2SO_4 decomposition section development is now focusing on the integrated SiC bayonet heat exchanger concept to mitigate the corrosion and complexity issues of the previous systems. The initial tests performed in the ceramic decomposer confirmed calculated values for SO_2 conversion and heat recuperation. The HI and H_2SO_4 section development will be completed in early FY 2007. The HI and H_2SO_4 sections will be integrated with the French CEA Bunsen section and assembled into an integrated experiment late in FY 2007. Integrated lab-scale experiments are planned for FY 2008.

Publications

1. Fred Gelbard, Robert C. Moore, Milton E. Vernon, Edward J. Parma, Dion A. Rivera, James C. Andazola, Gerald E. Naranjo, Carlos E. Velasquez, and Andrew R. Reay, "Pressurized Sulfuric Acid Decomposition Experiments for the Sulfur-Iodine Thermochemical Cycle" World Hydrogen Energy Conference, June 2006, Lyon, France.
2. Fred Gelbard, Robert C. Moore, Milton E. Vernon, Edward J. Parma, Dion A. Rivera, Howard B. J. Stone, James C. Andazola, Gerald E. Naranjo, and Paul Pickard, "Sulfuric Acid Decomposition with Heat and Mass Recovery using a Direct Contact Exchanger," AIChE Annual Meeting, San Francisco, California, November, 2006.
3. Bunsen Wong, et.al., "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE Spring Meeting, April 2005, Atlanta, GA.

4. 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.
5. Paul M. Mathias, Lloyd C. Brown, "Quantitative Analysis of the Sulfur-Iodine Cycle Through Process Simulation," AIChE Spring Meeting, April 2005, Atlanta.
6. Paul M. Mathias, Lloyd C. Brown, "Phase Equilibria and Thermodynamic Properties of the Sulfur-Iodine Cycle," AIChE Spring Meeting, April 2005, Atlanta, GA.

Presentations

Numerous presentations on the S-I project have been given by project participants including:

1. NHI Semiannual Review Meetings (November 2005, March 2006).
2. US French INERI Review Meetings (France, June 2005, U.S., January 2006).