II.H.1 Sulfur-Iodine Thermochemical Cycle

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Start Date: September, 2002
Projected End Date: April, 2009 (completion of lab scale experiments)

Objectives

- Evaluate the potential of the Sulfur-Iodine (S-I) thermochemical cycle for large-scale hydrogen production using nuclear energy.
- Perform an integrated lab-scale (ILS) experiment to demonstrate closed-loop operation of the S-I cycle.
- Provide the technical basis for the DOE Nuclear Energy assessment of the S-I cycle for thermochemical hydrogen production using advanced nuclear reactors.

Technical Barriers

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

- Process chemistry and thermodynamic data information for evaluation of S-I cycle efficiency and operational characteristics.
- High-temperature, corrosion resistant materials for extended service under thermochemical process conditions.
- Thermochemical hydrogen production economics.

Approach

- Flowsheet analysis of the S-I cycle process to evaluate alternative configurations.
- Experiments to investigate the chemistry of the three major reactions for the S-I cycle.
- Develop improved materials and heat exchanger designs for service in high temperature corrosive environments.
- Design and construct an ILS apparatus to provide a test bed for S-I cycle evaluation.
- Perform ILS experiments to evaluate closed loop operation.
- Develop system designs, sizing, and materials for a nominal MW pilot scale experiment.

Accomplishments (through May 2008)

The first hydrogen production experiment using CEA Bunsen section feed material was completed in April 2008. The acid decomposition section and the Bunsen section were operated together to produce and separate the HIx (heavy) phase and H_2SO_4 (light) phase acids. After analysis, the hydrogen iodine (HI) decomposition section was run using the HIx feed material from the CEA section to produce hydrogen at a nominal 50 l/hr. The HI section operation demonstrated all process operations for that section including iodine extraction, HI distillation, decomposition, and HI recycle. The CEA SO_2/O_2 separation section operated reliably in multiple operations. The high temperature acid decomposition section incorporates acid vaporization, decomposition, and recuperation in one integrated SiC bayonet unit, with no corrosion issues identified in multiple test series. Acid decomposition experiments have been performed at a range of conditions: temperatures up to 850°C, pressures to 5 bar, and production rates up to 300 l/hr SO_2 at 40 mole%. SO_2 conversion at ILS flow rates is ~90% of theoretical.

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Introduction

The U.S. DOE and the French CEA are investigating the S-I thermochemical cycle as one of the promising methods for production of hydrogen from advanced nuclear reactors. The focus of this collaborative effort is the construction and operation of an ILS experiment that will provide the technical basis for the evaluation of this cycle. The ILS experiment will investigate the operational characteristics, performance potential and provide input for the cost implications of this cycle to support future technology selection decisions for nuclear hydrogen production. The ILS for S-I is being conducted as an INERI project and is a collaborative effort involving Sandia National Laboratories (SNL), General Atomics, and the French CEA. The CEA is designing and testing Section 1, the primary (Bunsen) reaction section. General Atomics is developing and testing Section 3, the HI decomposition section. SNL is developing and testing Section 2, the high temperature H_2SO_4 decomposition section.

Status

The three primary chemical process sections have been assembled and integrated at the General Atomics site and integrated testing is underway (Figure 1). The three sections are connected through an interface unit that provides a set of supply and receiver tanks for each of the primary process streams that allows independent operation of each section in stand alone mode, but allows coupling of the supply and receiver tanks for fully integrated operations.

Results

The objective of the Phase 1 tests (October 2007 though April 2008) was to establish the capability for integrated operations and demonstrate hydrogen production from the S-I cycle. This objective was achieved during the Phase 1 tests with the successful integrated operation of the SNL acid decomposition and CEA Bunsen reactor sections to produce the required heavy and light acid phase product streams. In this operation, the O_2/SO_2 gaseous mixture generated by the SNL acid decomposer is compressed to separate the O_2 and produce liquid SO_2 for the Bunsen reaction. Iodine from the interface unit was sent to the Bunsen reactor and mixed with the sulfur dioxide being generated by the sulfuric acid decomposition skid. SO_2 and water are introduced at the bottom of the Bunsen reactor and iodine is pumped into the top in a counterflow configuration. The resulting light phase produced (H_2SO_4) was returned to the interface unit, and the heavy phase HIx produced (Figure 2) was collected for chemical analysis and subsequent processing in the HI decomposition section. Although control of the feed flow rates must be improved to optimize product concentrations, this operation successfully produced and separated heavy and light acid phases for subsequent processing.

Additional hydriodic acid was added to the Bunsen section heavy phase to provide sufficient volumes, and the solution was then processed by the HI decomposition skid to produce hydrogen and iodine. Figure 3 shows the hydrogen production for the integrated run which utilized the lower phase produced by the CEA Bunsen section. The initial spike in the H_2 flow is characteristic of the initial saturation of the HI reactor and break through of material as the reactor reaches equilibrium flow conditions. The subsequent decline and then stabilization corresponds to the period of sustained, steady-state operation.

Several subsystems within the HI skid were successfully demonstrated during this integrated experiment with a maximum hydrogen production rate of ~50 liter per hour. This is the first time the S-I cycle has been constructed using engineering materials and operated at prototypic temperature and pressure to produce hydrogen.

Conclusions and Next Steps

The results of the first integrated test identified areas of modification or improvement that will be implemented in future testing. Additional diagnostics will be added to the Bunsen reactor vessel to improve the quality and consistency of the chemicals

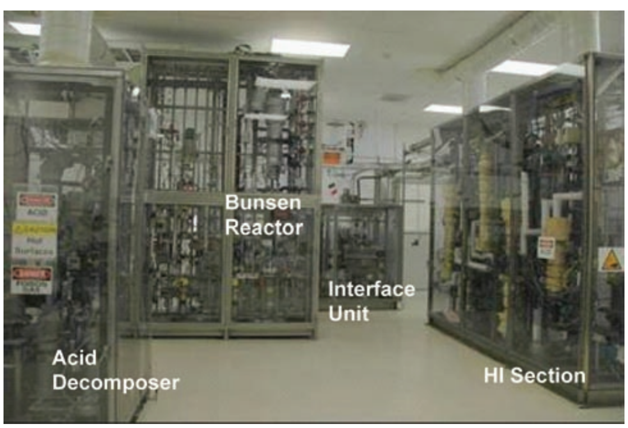

FIGURE 1. The DOE-CEA S-I ILS Experiment Installed at the General Atomics Lab-Scale Test Facility Site

FIGURE 2. HIx Collected in Skid 1 at the Exit of the Bunsen Reactor

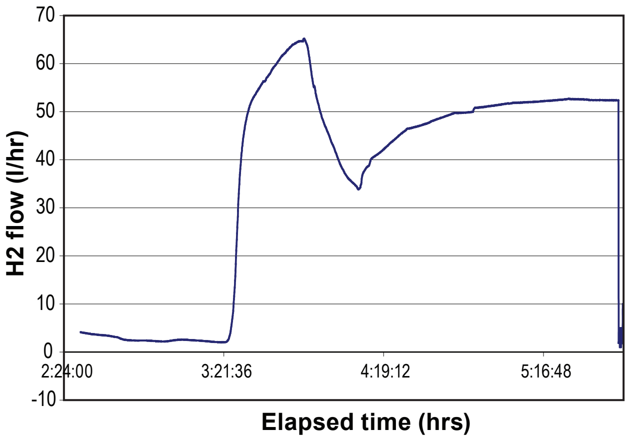

FIGURE 3. Hydrogen Production Rate for the Initial S-I Cycle Integrated Run (April 2008)

produced. The CEA anticipates that most hardware modifications will be completed in Fiscal Year 2008. The HI decomposition reactor will be replaced with a smaller unit to facilitate control and response times for the HI section. Evaluation of the durability of the materials of construction for the HI section will also be conducted and modifications implemented based on that evaluation. With the initial integrated test complete, preparations for the next phase operations are underway and will be completed in FY 2008. The first half of FY 2009 will focus on optimizing Bunsen and HI section operations, and completing the assessment of the integrated S-I cycle operations.

FY 2008 Presentations

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

1. NHI Semiannual Review Meetings (October 2007, March 2008).
2. U.S.-French INERI Review Meetings (January 2008).

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