An Integrated Laboratory-Scale Experiment on the Sulfur – Iodine Thermochemical Cycle for Hydrogen Production

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Abstract

Sandia National Laboratories (SNL), General Atomics Corporation (GA) and the French Commissariat à l'Energie Atomique (CEA) have been conducting laboratory-scale experiments to investigate the thermochemical production of hydrogen using the Sulfur-Iodine (S-I) process. This project is being conducted as an International Nuclear Energy Research Initiative (INERI) project. In the S-I process, 1) H_2SO_4 is catalytically decomposed at high temperature to produce SO_2, O_2 and H_2O. 2) The SO_2 is reacted with H_2O and I_2 to produce HI and H_2SO_4. The H_2SO_4 is returned to the acid decomposer. 3) The HI is decomposed to H_2 and I_2. The I_2 is returned to the HI production process. Each participant in this work is developing one of the three reaction sections. SNL is constructing the H_2SO_4 decomposition section, CEA, the HI production section and General Atomics, the HI decomposition section. The objective of initial testing of the S-I laboratory-scale experiment was to establish the capability for integrated operations and demonstrate H_2 production from the S-I cycle. This objective was achieved during the Phase 1 tests with the successful integrated operation of the SNL H_2SO_4.acid decomposition and CEA Bunsen reactor sections and the subsequent generation of H_2 in the GA HI decomposition section. This is the first time the S-I cycle has been realized using engineering materials and operated at prototypic temperature and pressure to produce hydrogen.

INTRODUCTION

As part of the US DOE Nuclear Hydrogen Initiative, an international collaborative effort between Sandia National Laboratories (SNL), General Atomics Corporation (GA) and the French Commissariat à l'Energie Atomique (CEA) has been undertaken for constructing and testing a laboratory-scale thermochemical Sulfur-Iodine (S-I) process (Norman et al., 1982; Sakurai et al., 1999) for the production of hydrogen from water. This project is being conducted as an International Nuclear Energy Research Initiative (INERI) project. The integrated experiment is being performed at the General Atomics facility in San Diego, CA. The objective of the program is to demonstrate thermochemical hydrogen production at a rate of 100 to 200 L/hr in a process utilizing scalable technology that enables the design of a larger pilot-scale process in the future. The key issues addressed in this project include selection of construction materials, characterization of individual chemical process operations, and process control and

technology scalability. Each participant has developed one of the three major process sections of the S-I process. To date, each process section has been constructed, tested and operations in an integrated mode have been initiated.

The S-I process consists of three chemical reactions coupled together to form a cycle where the inputs are heat and water and the outputs are O_2 and H_2. All other chemicals used in the process are regenerated and recycled. The three reactions are:

$$H_2SO_4 \text{ Decomposition: } H_2SO_4 \rightarrow SO_2 + H_2O + O_2 \quad (1)$$

$$\text{HI Production (Bunsen Reaction): } SO_2 + I_2 + H_2O \rightarrow HI + H_2SO_4 \quad (2)$$

$$\text{HI Decomposition: } HI \rightarrow H_2 + I_2 \quad (3)$$

The decomposition of H_2SO_4 is performed at approximately 850ºC in the presence of a catalyst. O_2 is a byproduct of the reaction. The production of HI, known as the Bunsen reaction, is exothermic and performed at approximately 5 bar and 120ºC. HI is decomposed at 400ºC and 10 bar. The high-temperature heat source can be nuclear, solar or another high-temperature source. The major advantages of the S-I process is the potential for high efficiency with most of the energy needed being thermal, and the relatively more advanced development status of the sulfur cycle.

The three sections of the S-I process have been constructed on skids with Lexan enclosures. The process sections are integrated through a chemical storage or buffer skid. With the exception of SO_2, all chemicals used in the S-I process are transferred to and from the chemical storage skid. For safety reasons, SO_2 gas is transferred directly from the acid decomposition skid to the HI production skid. The chemical storage skid allows for each section of the S-I process to operate in the stand alone or integrated mode.

This report summarizes results of the initial integrated testing of the lab-scale S-I process. SO_2, produced in the acid decomposition section, was transferred directly to the Bunsen section where it was reacted with I_2 and H_2O from the chemical storage skid. The resulting H_2SO_4 and HI products were transferred to the central storage skid for use in the acid decomposition section and hydrogen iodide decomposition sections. The HI was then decomposed to produce H_2 and I_2. The I_2 was transferred to the central storage skid for reuse in the Bunsen section. The acid decomposition and Bunsen sections operated simultaneously in an integrated mode, but the HI decomposition section was operated one day later to allow analysis of the HI product from the Bunsen section before proceeding. The initial integrated operation demonstrated the ability to successfully operate each process section and transfer chemicals between the sections.

PROCESS DESCRIPTION

Hydrogen Iodide Production (Bunsen Section)

The HI production section known as the Bunsen section (Fig. 1) performs two primary process functions: Separation of O_2 from the $SO_2/O_2/H_2O$ stream received from the acid decomposition section and the reaction of SO_2, H_2O and I_2 to form HI and H_2SO_4. The $SO_2/O_2/H_2O$ mixture is collected in a buffer tank where the H_2O is cryogenically removed. The remaining SO_2/O_2 mixture is compressed to liquefy the SO_2. The O_2 remains gaseous and is first scrubbed with H_2O to remove any residual SO_2 and then vented. The liquid SO_2 is transferred to the chemical reactor (Bunsen reactor) where it is combined with I_2 and H_2O to produce HI and H_2SO_4. The Bunsen reaction is exothermic and is performed in a counter current three phase reactor at ~120 °C and 6 bar. The heavy phase from the Bunsen reaction exiting the bottom of the reactor contains mainly HI whereas the light phase exiting the top of the reactor contains mainly H_2O and H_2SO_4

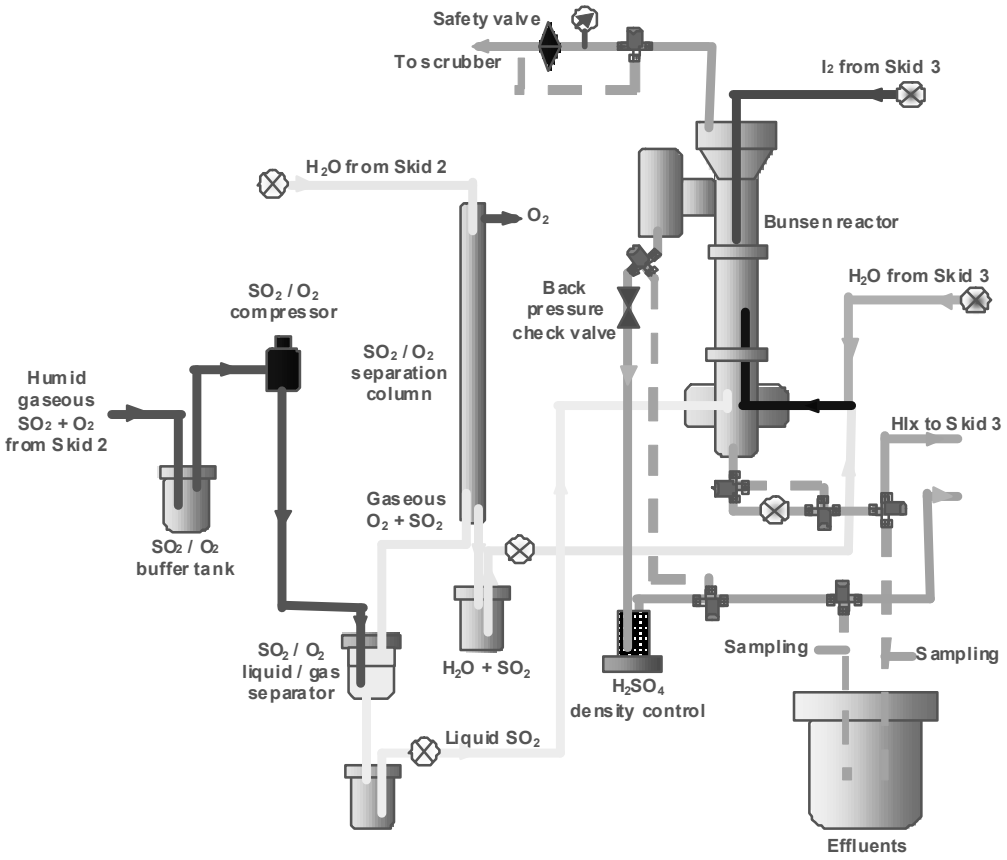

Fig. 1. Schematic diagram of the HI production or Bunsen section of the S-I process

Sulfuric Acid Decomposition

A schematic of the H_2SO_4 decomposition process is shown in Fig. 2. Two main chemical processes in this section are the concentration of dilute H_2SO_4 received from the Bunsen process and the thermal-catalytic decomposition of H_2SO_4 to produce SO_2, H_2O and O_2. Incoming acid from the Bunsen process is ~20 mole % and is concentrated to 40 mole % in a thin film type evaporator operated under vacuum. The evaporator is constructed of silicon carbide and Teflon. Preconcentration of the acid before decomposition is not a requirement, but allows the acid decomposer to operate at higher capacity. The concentrated acid is fed to the acid decomposer where it is decomposed at 850ºC in the presence of a platinum catalyst. The acid decomposer is an all ceramic bayonet type heat exchanger constructed of concentric silicon carbide tubes with a catalyst placed in the top section of the apparatus. Detailed descriptions of the acid concentrator and decomposer are given elsewhere (Moore, et al. 2007; Helie, et al. 2007). Any undecomposed acid is collected at the exit of the acid decomposer for recycle. The product stream, SO_2, H_2O and O_2, is passed through a water chilled condenser at 5ºC to remove most of the H_2O to avoid corrosion in the current piping. The H_2O is transferred to the chemical storage skid and the SO_2, O_2 mixture is transferred directly to the Bunsen section.

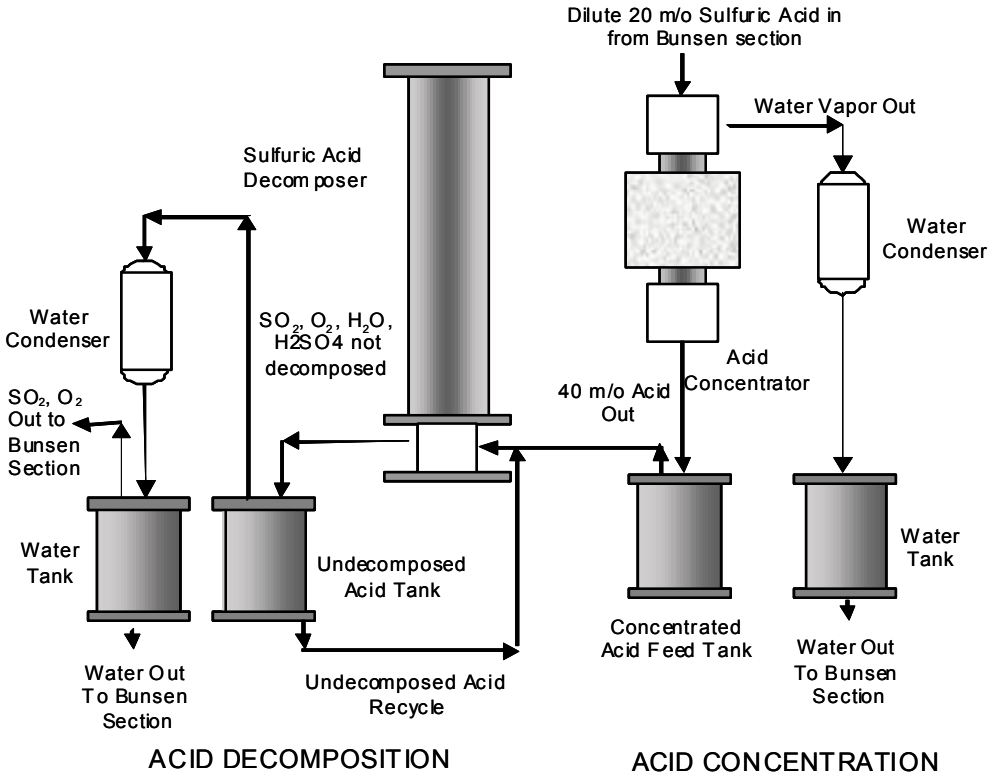

Fig. 2. Schematic diagram of the sulfuric acid decomposition section for the S-I process

The acid decomposer is operated at a pressure of 2 bars or greater. Pressure is maintained with a Teflon (Equilibar, Inc.) backpressure regulator placed at the product exit of the process. The backpressure regulator effectively isolates the acid decomposer from any

pressure fluctuations created by cycling of the gas compressor in the Bunsen section. PTFE/glass rotameters (Cole Parmer) are used to monitor the flowrate of acid feed and recycle acid to the acid decomposer. The composition of the product gas stream is monitored with an O_2 analyzer (Oxygraf, Inc.) and the flowrate is determined with a flowmeter constructed of Ryton (McMillan, Co.).

HI Decomposition Section

The HI decomposition process system (Fig. 3) consists of 6 major chemical processes: I_2 extraction, HI distillation, HI decomposition, iodine recycle, HI recycle and phosphoric acid concentration. The HI decomposition skid receives HI feed, 2:8:10 molar ratios of $HI:I_2:H_2O$, from the HI production process and first removes the I_2 in a liquid-liquid extraction process utilizing H_3PO_4 acid to break the HI, H_2O azeotrophe. The HI is distilled from the remaining H_2O, H_3PO_4 solution and pumped to the reactor for decomposition to I_2 and H_2. As the reaction is thermodynamically limited to 20% conversion, the unreacted HI must be separated and recycled in order to reach the desired H_2 production rates. Any undecomposed HI in the product stream is cryogenically separated from I_2 for recycle of the HI back to the reactor. The cryogenic method can recover up to 90% of the unreacted HI. The material of construction for the plumbing and process vessels is mainly a tantalum-10% tungsten alloy. This material was selected based on its corrosion resistance as well as its flexibility for plumbing. The main process vessels are 2" diameter tube with the process lines 0.5" tubing. Tantalum coated Swagelok fittings were used for process line connections.

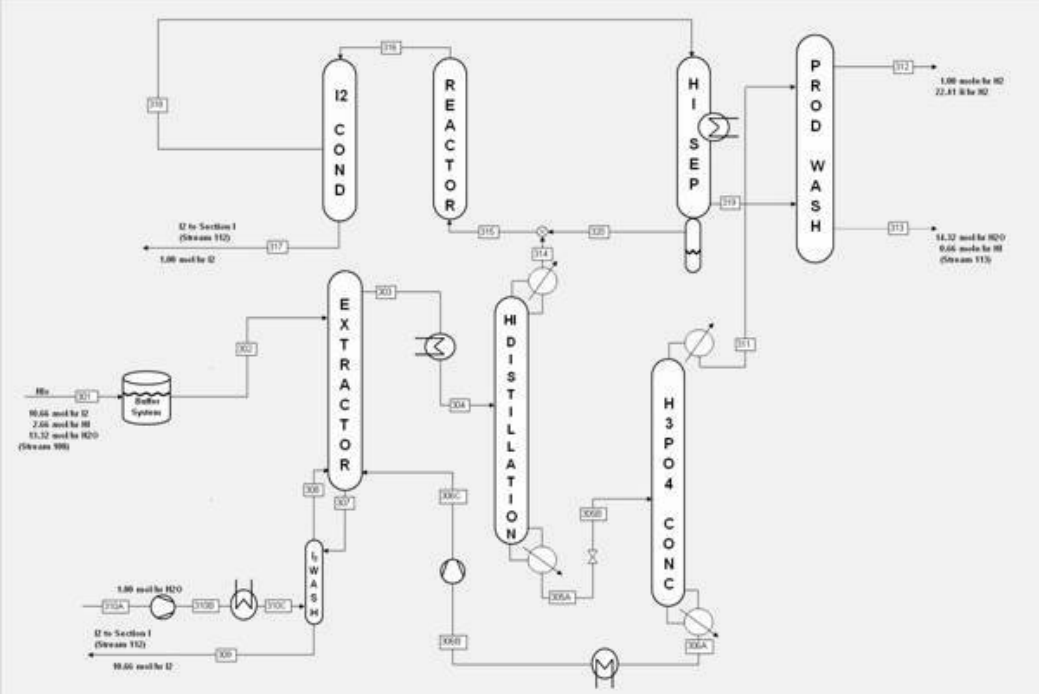

Fig 3. HI decomposition process for the S-I process

Process Integration

As previously stated, integration of the three sections of the S-I process is through a chemical storage or buffer skid. A picture of the S-I process with the three process sections and the chemical storage skid is given in Fig. 4. The chemical storage skid, only partially visible in the back, houses Teflon lined stainless steel tanks for H_2SO_4 and H_2O and heated glass lined steel tanks for HI and I_2. A chemical scrubber is also located on this skid for disposal of any unwanted chemicals produced in stand alone or integrated testing.

Fig. 4. S-I process showing three chemical process skids and chemical storage skid. From the left, the acid decomposition skid, the Bunsen process skid, the chemical storage skid (only partially visible in the back) and the hydrogen iodine decomposition skid

INTEGRATED OPERATION

The initial integrated testing was performed for approximately two hours with the H_2SO_4 decomposition section, the Bunsen section and the chemical storage skid. After chemical characterization of the HI product from the Bunsen section, the HI decomposition section was operated the next day to generate H_2.

Integrated testing consisted of transferring dilute H_2SO_4, 20 mole %, from a storage tank on the chemical storage skid to the acid decomposition skid. The acid concentrator and acid decomposer had been previously preheated to their operational temperatures of 180ºC and 850ºC (outside wall temperatures) respectively. The acid decomposer was slowly preheated to 850ºC over a period of four hours. The dilute acid was passed

through the acid concentrator and samples were collected from the exit stream during operation. Gravimetric analysis of the exiting acid indicated it was ~38 mole %. The concentrated acid was used to feed the acid decomposer at a flowrate of 9.0 ml/min. and SO_2 was generated at a rate of 116 L/hour. The ratio of SO_2/O_2 in the product stream was ~2:1. The SO_2, O_2 mixture was transferred to the Bunsen section and compressed to 10 bars to liquefy the SO_2. The liquid SO_2 was collected in a storage vessel and fed to the Bunsen reactor operated at 120ºC and 6 bar gauge. Iodine, contained in a heated vessel at 140ºC, located on the chemical storage skid and under a pressure of 4 bar gauge and H_2O also located on the chemical storage skid were transferred to the Bunsen reactor. The flowrates of these inputs were determined using calibration curves determined for each transfer pump. The light phase exiting the top of the reactor, consisting of H_2SO_4 and H_2O, was transferred to the chemical storage skid and analyzed. The heavy phase exiting the bottom of the reactor, consisting of HI, was transferred to a heated, 130ºC, glass lined vessel on the chemical storage skid for use in the HI decomposition section.

For the HI decomposition section, tests were initiated by pre-heating all units and process lines to their operational temperatures. The HI decomposition reactor was preheated to 450 ºC centerline temperature. The feed solution is then introduced into the skid storage tanks where it is pressurized and passed through the system. The feed is subsequently mixed with concentrated phosphoric acid, 92-96 weight %, stripping the I_2 away in the distillation column that was operated at 175 to 200ºC and a pressure of 5 bar. The remaining extract is then distilled, producing the HI gas which is fed to the main reactor that was operated at 450ºC and 10 bar. The density and liquid levels of the various fluids are monitored and controlled using Rosemount differential pressure cells. The temperature profile of the reactor is monitored, as the adsorption front of HI moves along the column. The hydrogen product was measured with a Flowmetrics, Inc. rotary meter and the H_2 concentration was determined using a H_2 Scan hydrogen sensor.

RESULTS AND DISCUSSION

The initial integrated operation of the S-I process demonstrated that with the current process configuration the three process sections can be successfully operated and chemical components can be transferred between the process sections or by means of a chemical storage skid. However, several problems were encountered and the resulting lessons learned in this work included proper conditions for transferring chemicals between processes, corrosion issues and monitoring and control issues.

In the sulfuric acid decomposition process, the acid concentrator and acid decomposer performed within design specifications. Fig. 5 is the output of SO_2 during the integrated operation. The decomposition of H_2SO_4 in the acid decomposer was 73% which is approaching the theoretical limit of 77 % at 850 C. There were no issues with corrosion during integrated operation as the use of silicon carbide and Teflon in the construction of the acid concentrator and decomposer has virtually eliminated corrosion problems in this process section. In earlier tests, problems existed with acid chugging in the acid decomposer due to cycling of the compressor in the Bunsen process. This problem was

eliminated by the addition of the backpressure regulator to maintain a constant pressure in the acid decomposition section and placing a 8 L buffer tank in the gas stream.

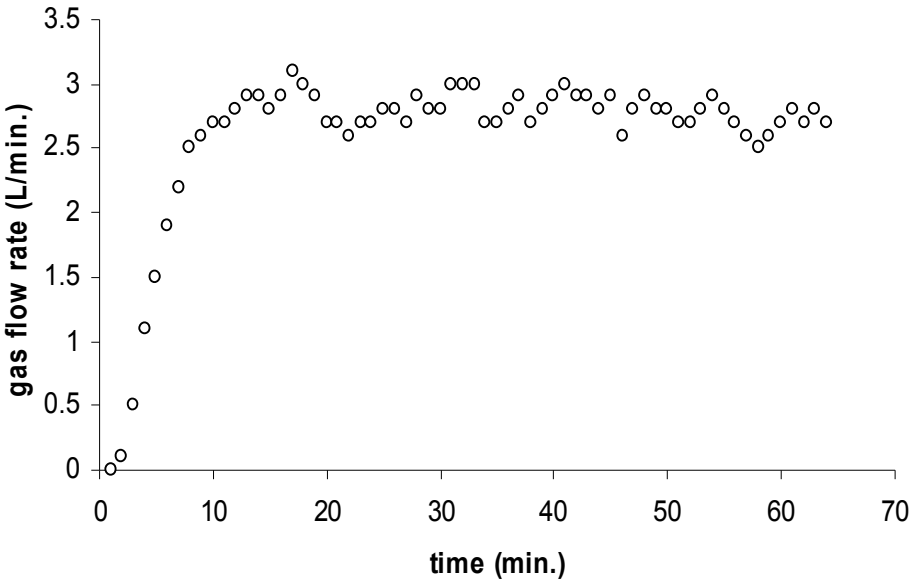

Fig. 5 SO_2 generation from the H_2SO_4 acid decomposition section as a function of time

Initially there were difficulties in transferring iodine as liquid at 130ºC from the chemical storage skid to the Bunsen reactor. This was not unexpected. Even minor cold spots in the I_2 stream result in freezing and plugging. A significant effort was required to ensure proper heating and insulation of the I_2 storage tank, pump and transfer line. A major issue still exists with the iodine pump. The high density and viscosity of I_2 at a temperature of 130ºC makes pumping on the very small scale encountered in this work very difficult. A more suitable pump for this task is being pursued but the problem has been mitigated for these initial operations by pressurizing the I_2 supply tank to ~4 bars. Additionally, accurate flowmeters are needed for better control over the Bunsen reactor. We are currently examining various options for pumps and flowmeters including gear type positive displacement pumps and flowmeters constructed of tantalum or coated with a refractory metal.

An analysis of the heavy phase exiting the Bunsen reactor indicated the composition was 42 wt % HI and 10 wt% I_2. The light phase contained considerable amounts of HI and I_2. After removal of these components the density was determined to be 1.23 g/cm^3. The target value is 1.5 g/cm^3 that corresponds to 20 mole % H_2SO_4. The results indicate that although the reaction did occur, the Bunsen reactor was not operating at optimum conditions. This was most likely due to uncertainty in the flowrates of reactants to the reactor. We anticipate the installation of new, more accurate flowmeters will correct this problem. In addition to improving control over chemical inputs to the Bunsen reactor it is theorized that better mixing is needed in the reactor. Therefore, Raschig rings will be

placed in the reactor above the SO_2 inlet to improve mixing of SO_2 and H_2O in this section. Also, major modifications will be made to the reactor to accommodate differential pressure transducers to allow for better monitoring and control over the interface level between the heavy and light phases.

Fig. 6 shows the internal temperature profile of the HI reactor during operation. What is observed is a temperature front moving through the reactor. Thermocouple TT_300D is located near the entrance of the reactor, thermocouple TT_300C in the middle zone, and thermocouple TT_300B near the exit of the reactor. The temperature front is a result of the reactor reaching equilibrium with respect to the absorption/desorption of the HI gas onto the activated carbon catalyst and subsequent reaction to form H_2 and I_2. Shortly after the temperature front passed the location of thermocouple TT_300B at the reactor H_2 was detected in the exit stream.

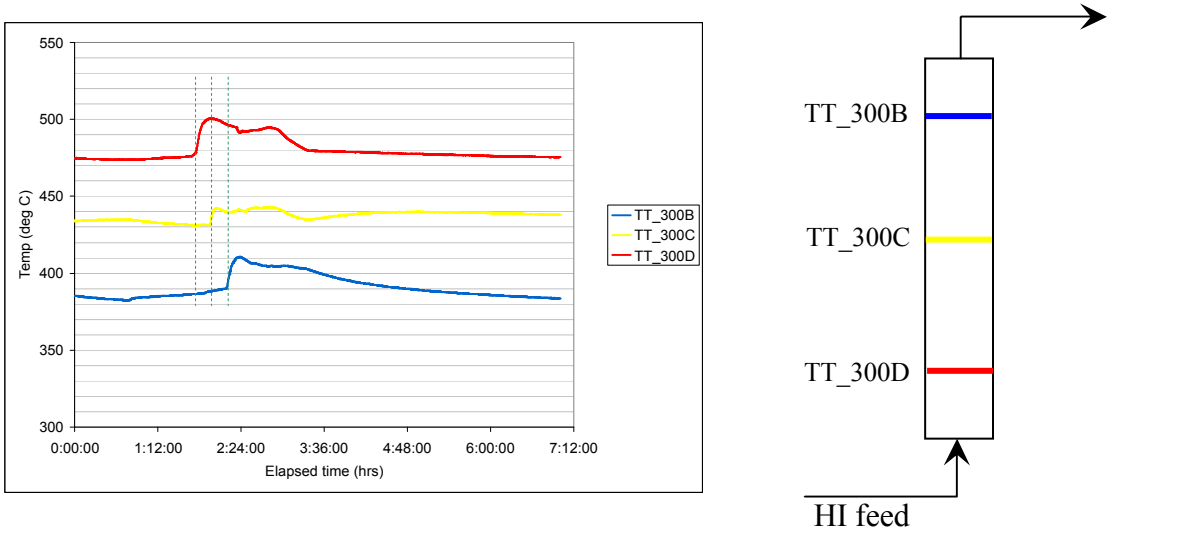

Fig. 6 Temperature profile in the HI decomposition reactor during HI saturation.

The effect of the recycle unit in the HI decomposition section was to triple the production rate of H_2. Table 1 summarizes the results of HI recycle for the integrated operation. Of the input flow rate of 17mol/hr, only about half is distilled to the reactor due to the simple distillation column used in this experiment. Of the nominal 8.5 mol/hr distilled to the reactor, only about 10% is predicted to decompose to H_2 and I_2 at these conditions. The recycle of undecomposed HI results in a factor of three increase in the H_2 production rate which is consistent with predictions for 5 bar.

Table 1. Results for HI recycle in HI decomposition process

HI feed in HIx	17 mol/hr
HI distilled to reactor	8.5 mol/hr
Predicted H_2 produced with no recycle	0.85 mol/hr (19 l/hr)

H_2 actually produced	2.7 mol/hr (60 l/hr)

Fig. 7 shows the hydrogen production for the integrated run which utilized the lower phase produced by Section 1. The initial transient in the H_2 flow is characteristic of the initial H_2 signal as the HI saturates the reactor and the reactor reaches equilibrium. The subsequent decline and then stabilization corresponds to the period of sustained, steady-state operation.

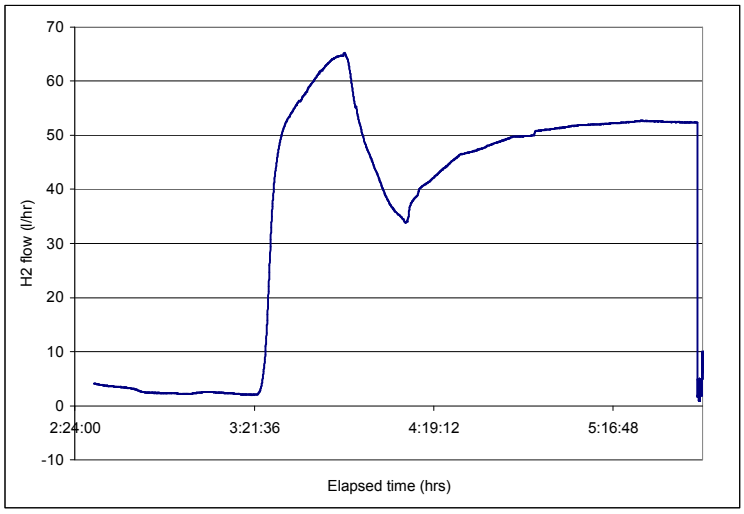

Fig. 7 Hydrogen production rate for the integrated S-I process operation

Additional integrated testing is to take place in the near future after modifications to the Bunsen section have been completed.

CONCLUSIONS

The objective of initial testing of the S-I laboratory-scale experiment 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, and the subsequent generation of hydrogen from that material in the HI decomposition section. Although this operation successfully produced and separated the expected heavy and light acid phases, control of the feed flow rates to the Bunsen reactor must be improved in the next phase of testing to optimize the composition of the output phases. The heavy phase material subsequently processed in the General Atomics HI decomposition produced hydrogen at the expected rates. 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.

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