This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

The Hybrid Sulfur Cycle for Nuclear Hydrogen Production

Proceedings of GLOBAL 2005
Tsukuba, Japan, Oct 9-13, 2005
Paper No. 097

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ABSTRACT: Two Sulfur-based cycles – the Sulfur-Iodine (SI) and the Hybrid Sulfur (HyS) – have emerged as the leading thermochemical water-splitting processes for producing hydrogen utilizing the heat from advanced nuclear reactors. Numerous international efforts have been underway for several years to develop the SI Cycle, but development of the HyS Cycle has lagged. The purpose of this paper is to discuss the background, current status, recent development results, and the future potential for this thermochemical process. Savannah River National Laboratory (SRNL) has been supported by the U.S. Department of Energy Office of Nuclear Energy, Science, and Technology since 2004 to evaluate and to conduct research and development for the HyS Cycle. Process design studies and flowsheet optimization have shown that an overall plant efficiency (based on nuclear heat converted to hydrogen product, higher heating value basis) of over 50% is possible with this cycle. Economic studies indicate that a nuclear hydrogen plant based on this process can be economically competitive, assuming that the key component, the sulfur dioxide-depolarized electrolyzer, can be successfully developed. SRNL has recently demonstrated the use of a proton-exchange-membrane electrochemical cell to perform this function, thus holding promise for economical and efficient hydrogen production.

KEYWORDS: *Hydrogen, thermochemical, Hybrid Sulfur, nuclear, electrolyzer, sulfur dioxide*

I. INTRODUCTION

The U.S. DOE (Department of Energy) Office of Nuclear Energy, Science, and Technology has created the Nuclear Hydrogen Initiative (NHI) program with the objective of advancing nuclear energy to support the future hydrogen economy. The NHI has been established to develop the technologies that can be most effectively coupled to next generation nuclear reactors for hydrogen production. Thermochemical water-splitting cycles, which use thermal energy to produce hydrogen through the dissociation of water molecules, are leading technologies that are being studied within the NHI program.

Research programs in the United States, Japan and France have emphasized the sulfur-based thermochemical cycles as high priority candidates for research and development. The NHI has identified the Sulfur-Iodine (SI) Cycle and the Hybrid Sulfur (HyS) Cycle as first priority baseline cycles. These cycles have potential for high efficiency, and they have been demonstrated at a laboratory-scale to confirm performance characteristics. Both cycles share a common high-temperature reaction step – the catalytic thermal decomposition of sulfuric acid. There has been considerable research and development performed in recent years related to the SI Cycle, including the high temperature acid decomposition step. Conversely, there has been little recent work on the HyS Cycle. The purpose of this paper is to present a discussion of the background and basics of the HyS Cycle, a conceptual design and performance estimates, key technical issues, and to present the results of a laboratory-scale development program that culminated in demonstration testing of the key component of the process, the sulfur dioxide depolarized electrolyzer (SDE).

II. BACKGROUND

The HyS Cycle is an all fluids cycle that involves a single electrochemical step and a single thermochemical step. As a two-step process, it is the simplest thermochemical process that has been demonstrated. The chemistry involves only sulfur compounds, water, hydrogen and oxygen. The two process steps are as follows:

$$SO_2 + 2\,H_2O \;?\; H_2\,? + H_2SO_4 \qquad (1)$$
(electrochemical, 80-120°C)

$$H_2SO_4\;?\; H_2O + SO_3\;?\; H_2O + SO_2 + ½O_2 \qquad (2)$$
(thermochemical, 800-900°C)

The net result of Reactions 1 and 2 is the decomposition of water into hydrogen and oxygen. All the sulfur compounds are regenerated and recycled as process intermediates.

Reaction 1 is performed in an electrochemical cell, similar to a water electrolyzer. Sulfur dioxide is dissolved in concentrated sulfuric acid (50-70 wt%) and is used to depolarize the anode of the cell, producing sulfuric acid, rather than oxygen, as the anode product. Hydrogen ions migrate across the electrolyte and produce hydrogen gas at the cathode. Previous work used a microporous rubber membrane to separate the cell compartments(1), whereas the current work uses a proton-exchange membrane (PEM). The theoretical reversible cell voltage required to dissociate water in an SDE with 50% acid feed operating at 25°C is 0.29 volts(1). This compares with a reversible cell voltage of 1.23 volts for direct water electrolysis. Thus, an SDE can potentially produce hydrogen using only 24% of the electricity required by water electrolysis. Of course, the sulfur dioxide must be regenerated by Reaction 2 in order to complete the HyS Cycle. The overall process efficiency, considering the total thermal energy needed to produce electricity for Reaction 1 and to conduct Reaction 2, is on the order of 50% (based on the higher heating value of the product hydrogen) for practical process configurations. Materials considerations, especially in the high temperature sulfuric acid section, are challenging. However, the absence of halides or other chemical species that are required in the other thermochemical processes eliminates the concern of cross-over contamination and simplifies the material requirements.

The Hybrid Sulfur Cycle, also known as the Westinghouse Sulfur Cycle or the Ispra Mark 11 Cycle, was originally developed in the early 1970's by Westinghouse Electric Corporation(2,3). In 1976, with DOE support, Westinghouse began work on a program to have a pre-pilot, integrated unit by 1983. All basic chemistry steps for the HyS Cycle were successfully demonstrated. By 1978, a closed-loop, integrated laboratory bench scale model was successfully operated producing 120 liters (STP) of hydrogen per hour(4). Work continued on equipment design and optimization, materials of construction, integration with a nuclear/solar heat source, process optimization, and economics until 1983. However, the ready availability of hydrogen from the steam reforming of natural gas at low prices, combined with reduced interest in developing either advanced nuclear reactors or high-temperature solar receivers, led to the termination of the work on this promising process.

In 2002, DOE supported a study to review all known thermochemical hydrogen production processes and to perform comparative evaluations of the leading contenders(5). The study cited eight hundred and twenty-two separate references in the world literature, and it identified 115 different unique cycles. These were evaluated against a set of numerical criteria and the HyS Cycle was ranked first. However, the study then performed a second screening in which it eliminated all hybrid processes from the selection list due to the perceived capital cost issues associated with electrolysis. The argument presented was that pure thermochemical processes could be more cost-effectively scaled-up to large nuclear plant capacities than processes that required an inherently modular step involving electrochemical cells. One of the primary goals of the current development efforts related to the HyS Cycle is to perform a comprehensive cost estimate in order to examine the issue concerning cost effectiveness.

III. DESCRIPTION OF THE ACTUAL WORK

A conceptual design for the HyS cycle was prepared and modeled using the AspenPlus™ process simulator. A flowsheet of the conceptual design was created, and material and energy balances computed. The plant consists of three major processing sections: 1) SO_2 anode-depolarized electrolysis, 2) sulfuric acid vaporization and decomposition, and 3) SO_2/O_2 separation. A simplified block schematic of the process is shown in Figure 1.

Preliminary estimates for the capital cost and the hydrogen production cost for an Nth-of-a-kind nuclear hydrogen production plant using the HyS cycle were prepared. The nuclear heat source design and cost prepared for a recent DOE study(6) using General Atomics Modular Helium Reactors and the SI thermochemical cycle were used as a cost basis. A commercial-scale plant design was developed consisting of four modular nuclear reactors combined with the thermochemical water-splitting process. Tradeoff studies were performed to determine the sensitivity of the hydrogen cost to changes in key process variables and capital cost estimates.

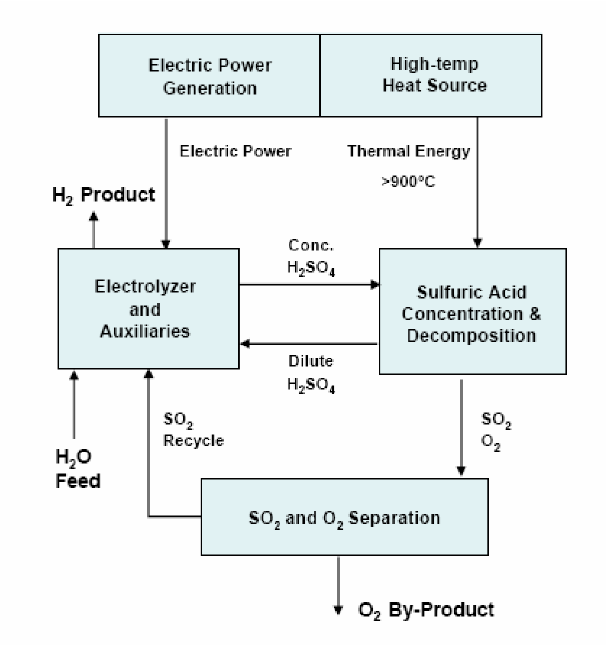

Figure 1. HyS Cycle Block Schematic

A research program was conducted to evaluate the technical issues and expected performance for an SO2-depolarized electrolyzer (SDE), the major developmental component of the HyS Cycle. The goal of the first year's efforts was to conduct proof-of-concept testing of an SDE utilizing technology similar to PEM water electrolyzers. Since proton-exchange-membrane technology is undergoing extensive development for use in automotive fuel cells, it was felt that this approach presented the best opportunity to develop an SDE meeting the necessary long-term cost goals of the program. A test facility for evaluating SDE was designed and constructed. Two separate PEM-type SDE's were constructed and tested.

IV. RESULTS

1. HyS Process Design and Performance

Several process improvements to the HyS flowsheet were developed during the course of the study. These included a more efficient means of concentrating and decomposing the sulfuric acid, an improved process for separating the sulfur dioxide and oxygen stream leaving the decomposition section and other overall process optimizations. A complete AspenPlus^{TM} flowsheet was prepared, and mass and energy balances were computed. The resultant overall net thermal efficiency for the HyS cycle was calculated as 48.8%, based on a peak thermal input temperature of 900°C. The efficiency was based on the higher heating value (HHV) of the hydrogen product divided by the total thermal energy requirements, including the thermal energy used to generate electricity and allowances for auxiliaries. Higher thermal efficiencies, exceeding 50%, are deemed feasible based on further process optimization and the use of a higher process operating temperature (requiring a higher nuclear reactor coolant outlet temperature). The design conditions selected for the process analysis are shown in Table 1.

Table 1. HyS Design Parameters

SO2-depolarized Electrolyzer	
Operating temperature, °C	100
Operating pressure, bar	20
H_2SO_4 concentration, wt%	65
SO_2 inlet concentration, wt%	8.95
Conversion per pass, %	50
Current efficiency, %	99
Avg. cell voltage, mV	525
Peak thermal input temperature, °C	900
Cooling water temperature, °C	25
Heat-to-electric efficiency for auxiliary power requirements, %	48

2. Cost Analysis

Hydrogen costs were based on a commercial nuclear hydrogen production plant rated at 2400 MW(th), comprised of four 600 MW(th) modular helium reactors$^{(6)}$. Due to the modularity of the reactors, the plant generated somewhat more electricity than the hydrogen plant required, resulting in the cogeneration of both hydrogen and electricity. Electricity production was assumed to be conducted at 48% thermal efficiency, representative of a gas-cooled nuclear reactor and a closed Brayton cycle power generation system$^{(7)}$. Plant output was 580 metric tonnes per day of hydrogen and 216 MWe. Estimated total installed capital cost for the nuclear reactor system, including power generation and high temperature heat supply system, was $1.2 billion. The total installed capital cost of the HyS Cycle equipment was $516 million, including $260 million equipment costs for the electrolyzer system.

The electrolyzer capital costs were estimated on a unit cost per square meter of electrolyzer cell active area. An overall cost estimate of this type was necessary since final electrolyzer design configurations are still unknown. Estimating cell costs based on active area was considered more accurate than using a cost per kilowatt basis due to the substantial differences in cell voltages and power densities between various applications, such as water electrolyzers, fuel cells and chlor-alkali cells. A baseline cost of \$2000 per square meter of active cell area was assumed. This can be compared to a current installed cost for chlor-alkali electrochemical cells of \$3500-7000 per m^2 and the cost goal of \$1025 per m^2 for advanced PEM water electrolyzer derived from the National Academy of Sciences(8) recommended cost goal of \$125 per kW. A further point of reference is the projected cost of PEM fuel cells for transportation applications. Although these costs reflect additional factors, such as mass production in very large numbers, it is interesting to note that a PEM fuel cell cost of \$50/kW translates into a cell cost of approximately \$350 per m^2, which is considerably less than the PEM electrolyzer cost goals. In order to determine the effect of different electrolyzer capital costs on the HyS hydrogen production cost, a sensitivity analysis covering a range of costs was performed.

The cost of hydrogen production for the HyS Cycle nuclear hydrogen production plant was determined to be \$1.60 per kilogram at the plant gate for the baseline case, including all nuclear fuel costs, capital recovery charges and operating and maintenance costs. This cost was \$1.77 for higher cost (\$3500 per m^2) electrolyzers and \$1.38 per kg for lower cost (\$1025 per m^2) electrolyzers. These costs can be compared to the hydrogen production costs for the SI nuclear hydrogen production plant given in Reference 6, which showed \$1.65 per kg for an assumed 52% plant efficiency. However, recent analyses indicate that the overall energy efficiency of the SI plant may be lower than the estimated value, resulting in a higher hydrogen production costs. An SI plant efficiency of 42% would increase hydrogen costs to approximately \$1.98 per kilogram. Hydrogen production costs for both the HyS and SI plants could be lowered if there is a market for the byproduct oxygen. Hydrogen costs with byproduct oxygen credit are \$1.31 per kilogram for the baseline HyS plant and \$1.36 and \$1.69 per kilogram for the SI plant with 52% and 42% efficiency, respectively.

3. Electrolyzer Development and Testing

The key technical issues for the HyS Cycle were evaluated, and no “show-stoppers” were identified. The unique research and development needs focus mainly on the electrolytic cell design and optimization. An electrolyzer test facility was designed and built in order to conduct proof-of-concept tests at room temperature and near atmospheric pressure. Future modifications will allow testing at higher temperature and increased pressure. A photograph of the one of the electrolyzers installed in the test facility is shown in Figure 2.

Figure 2. SDE installed in test facility.

Two slightly different SDE’s were designed, procured and tested. The first electrolyzer was based on a commercially available PEM water electrolyzer, with modifications to permit operation in the corrosive sulfuric acid environment of the SDE. The electrolyzer was built with Hastelloy B and Teflon wetted parts, a PEM electrolyte, and porous titanium electrodes. It had an active cell area of 86 cm^2, and a Pt catalyst loading of 4 mg/cm^2. It was recognized that the titanium electrodes would corrode in the SDE environment, but the manufacturer was unable to change this portion of the design. The second electrolyzer was assembled for SRNL by the University of South Carolina (USC). It was constructed with platinized carbon cloth electrodes, a Nafion 115 PEM electrolyte, carbon paper flow fields, and solid graphite back plates. The USC electrolyzer had an active cell area of 40 cm^2 and a Pt catalyst loading of 0.5 mg/cm^2. The absence of metal in the acid regions made the cell much more corrosion resistant than the commercial PEM cell.

Testing was conducted under various operating conditions using water and sulfuric acid feeds with and without sulfur dioxide. A major accomplishment was achieved by demonstrating sulfur dioxide depolarized electrolysis operation in both cells. SDE is evidenced by hydrogen production at the cathode and sulfuric acid production at the anode (witnessed by the absence of oxygen generation) and with cell voltages substantially less than the theoretical reversible voltage for straight water electrolysis (1.23 V). The test results showed cell voltages of less than 0.6 volts at low current densities at room temperature and near-ambient pressure. Open cell potential was less than 0.4 volts. The ability to utilize a PEM cell to perform SDE is a major step toward the goal of developing a cost-effective HyS hydrogen production system. Considerable development and cost reductions are occurring for PEM cells as a result of research on PEM fuel cells for automobiles. Many of the resultant improvements are expected to be adaptable to SDE operation.

One major design improvement required for using PEM cells for SDE is the limitation of sulfur dioxide crossover through the membrane to the cathode. This results in elemental sulfur formation and potential flow blockage and catalyst poisoning. SRNL's proof-of-concept tests did result in SO_2 crossover, but the sulfur was easily flushed from the cell and no catalyst poisoning was indicated. Future work will address means to reduce SO_2 crossover.

V. CONCLUSIONS

The major conclusions based on the work to date on the Hybrid Sulfur cycle are the following:

1. The HyS process is a viable thermochemical cycle which can achieve high thermal efficiency and low hydrogen production costs when combined with an advanced nuclear reactor.
2. SO_2-depolarized electrolysis is the key step in developing the HyS process.

3. Water electrolysis using PEM-type cell designs has been demonstrated under SO_2-depolarized conditions at low cell voltages (<0.6 VDC).

4. Further electrolyzer development is required to improve performance at high current densities by minimizing mass transfer resistance and limiting SO_2 crossover to the cathode.

5. An integrated laboratory model of the complete HyS cycle, including the electrolyzer and the acid decomposition system, is required to establish closed loop operation

ACKNOWLEDGMENTS

This work was performed by the Savannah River National Laboratory under U.S. Department of Energy Contract No. DE-AC09-96SR18500. Funding was provided by the DOE Office of Nuclear Energy, Science and Technology under the Nuclear Hydrogen Initiative, Work Package SR15TC21. Mr. David Henderson was the technical program monitor. His support and guidance are acknowledged and greatly appreciated.

NOMENCLATURE

DOE	Department of Energy
HHV	Higher Heating Value
HyS	Hybrid Sulfur
kW	kilowatt
m^2	square meters
MWe	megawatt electric
MW(th)	megawatt thermal
NHI	Nuclear Hydrogen Initiative
PEM	proton-exchange-membrane
Pt	platinum
SDE	sulfur dioxide depolarized electrolyzer
SI	Sulfur-Iodine
SRNL	Savannah River National Laboratory
STP	standard temperature and pressure
USC	University of South Carolina
V	volts
VDC	volts direct current

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