

Hybrid Sulfur Thermochemical Process Development

William A. Summers* and M. R. Buckner
Savannah River National Laboratory
May 23, 2005

***Presenter**

Project PDP45

This presentation does not contain any
proprietary or confidential information.

Overview

Timeline

- Start Date: June, 2004
- End Date: September, 2005
- 75% Complete
- Follow-on to complete integrated lab demo to be funded for 10/05 – 9/08

Budget

- Total funding (to date) - \$480 K
- FY04 Funding - \$180 K
- FY05 Funding - \$300 K
- FY06 thru FY08 - TBD

Barriers

- Electrolyzer performance and cost
- High temperature materials
- Lower nuclear H₂ cost than solar TC goal of \$3/gge at plant gate in 2015
- Proof-of-concept to meet MW-scale pilot plant decision by end of FY08

Collaborators

- Univ. of So. Carolina - Electrolyzer
- Westinghouse Electric - consultation
- Proton Energy Systems – PEM Elec.
- Sandia National Lab and INL – H₂SO₄ loop development & catalysts

Objectives

- **To assist DOE-NE in selecting the preferred Thermochemical Cycle for integration with an advanced nuclear reactor**
 - **Develop a conceptual design for the Hybrid Sulfur thermochemical hydrogen production system, including preliminary flowsheet analysis, estimated system performance, and projected hydrogen production costs**
 - **Identify key technical issues and concerns, and prepare a development plan for a fully-integrated laboratory demonstration of the HyS Cycle**
 - **Perform proof-of-principle demonstration testing of an SO₂ anode-depolarized electrolyzer using a single-cell PEM-type water electrolyzer under near-ambient conditions**

Technical Approach

- **Create a high-efficiency process design for the Hybrid Sulfur thermochemical water-splitting cycle**
 - Update and improve original Westinghouse flowsheets
 - Use AspenPlus software to calculate mass and energy balances and to optimize system performance and H₂ cost
- **Develop and test a high-performance PEM-based electrolyzer using SO₂ anode depolarization**
 - Leverage PEM fuel cell and electrolyzer advancements to develop a low-cost H₂O/SO₂ electrolyzer achieving cell voltages of <0.6 volts per cell
 - Perform small-scale proof-of-concept testing beginning with a modified PEM water electrolyzer
 - Characterize performance, materials integrity, sulfur crossover, and effects of operating conditions (temperature, pressure, acid concentration)

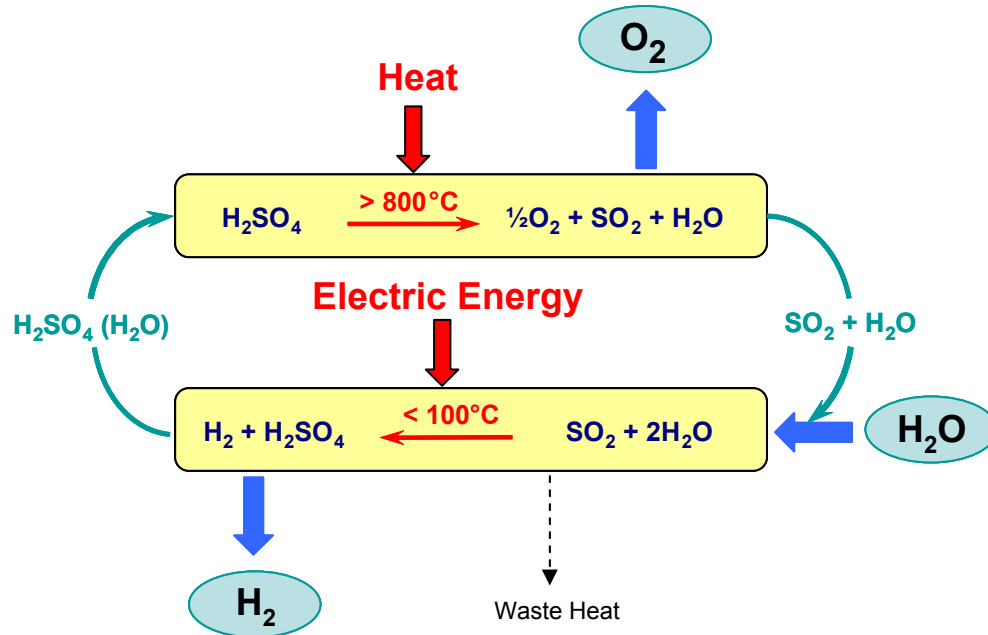
Accomplishments

- **Conceptual Design Report Completed (4/1/05)**
 - Improved system design with higher process efficiency of >50% (HHV)
 - SO₂-depolarized electrolyzer analysis performed; MEA/PEM concept selected; detailed development plan prepared
 - Key technical issues identified and approaches developed
 - Three patent disclosures prepared
- **Ambient Pressure Electrolyzer Testing**
 - Test plan prepared and issued
 - Test facility design completed; construction in progress
 - PEM-based SO₂-depolarized electrolyzer procured
- **Electrolyzer Development and Integrated Testing**
 - Integrated lab-scale test plan and conceptual design completed
 - High Pressure (20 bar) electrolyzer design scheduled for fourth quarter

Hybrid Sulfur Cycle

Inputs:

- Water
- Heat
- Electricity



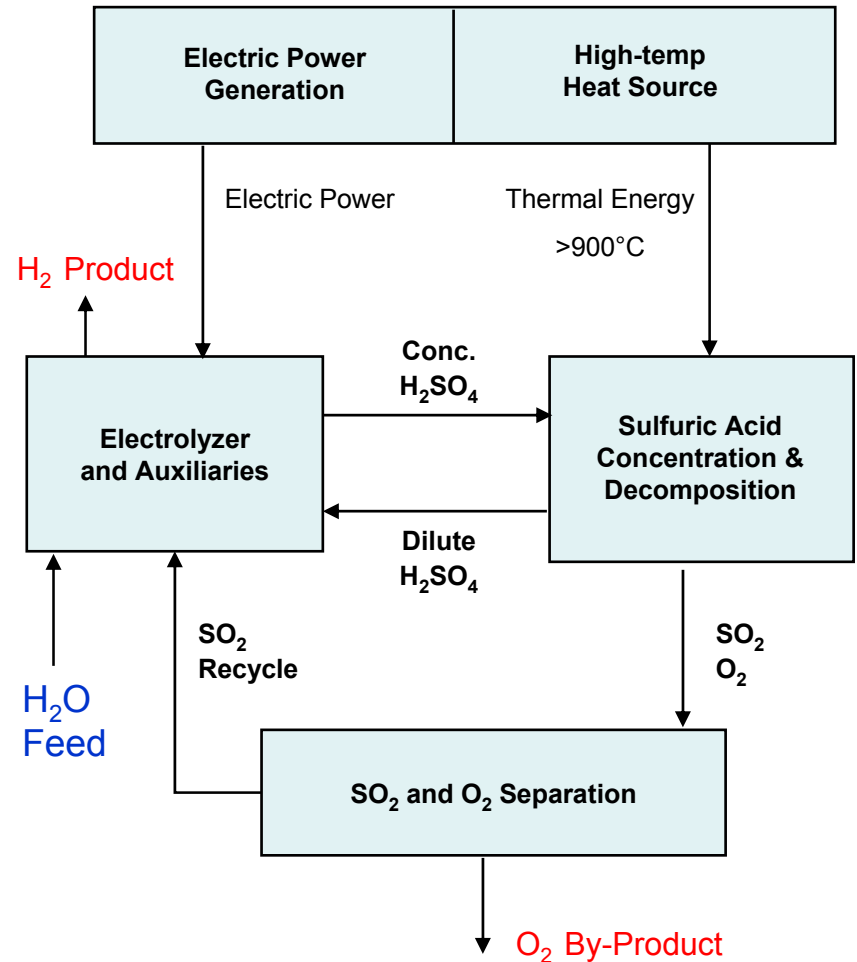
Outputs:

- Hydrogen
- Oxygen
- Waste Heat

- Originally developed by Westinghouse Electric in 1973-1983
- Two-step hybrid thermochemical cycle; only S-O-H chemistry
- SO₂ anode-depolarization reduces reversible cell voltage to 0.17 VDC per cell (more than 85% less than pure water electrolysis). Practical voltages are 0.45 to 0.60 VDC per cell.

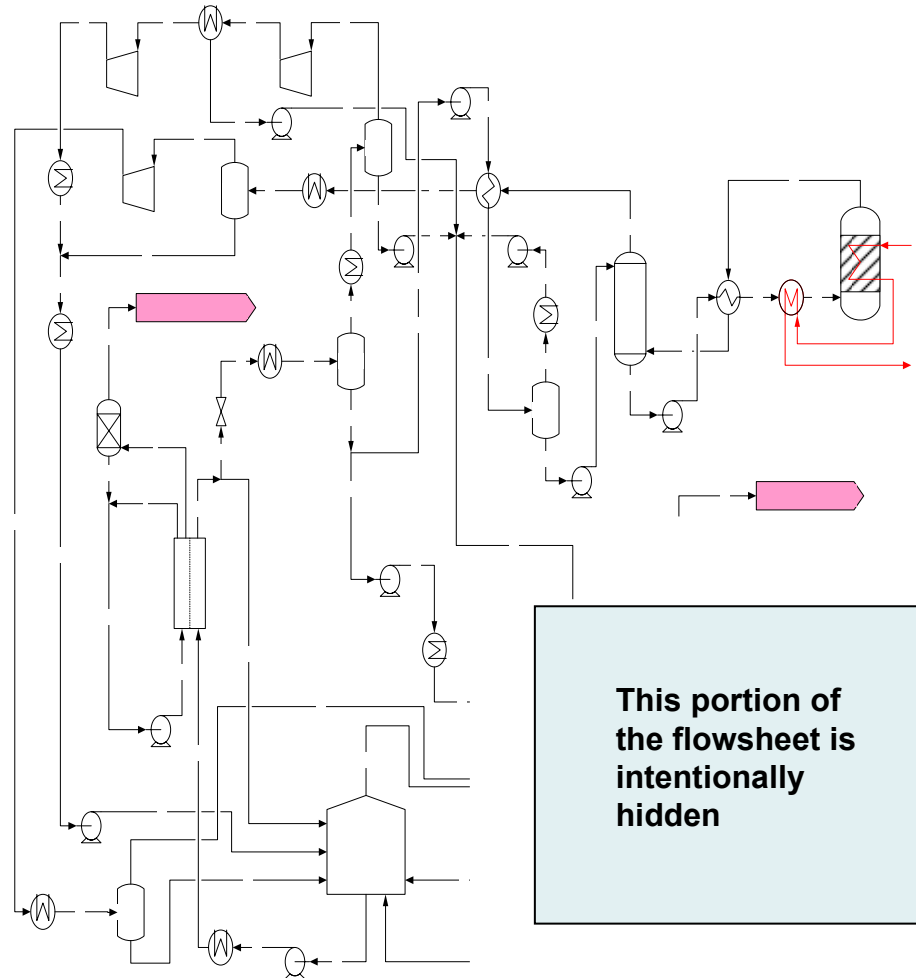
Processing Steps and Functions Defined

- High temperature ($>900^{\circ}\text{C}$) heat source could be nuclear reactor or solar thermal
- Thermochemical system has three main processing units
 - SO_2 -depolarized electrolyzers
 - Sulfuric Acid concentration and decomposition
 - SO_2/O_2 separation
- High Thermal Efficiency $>50\%$ (HHV basis) based on rigorous flowsheet modeling



Process Design Optimized

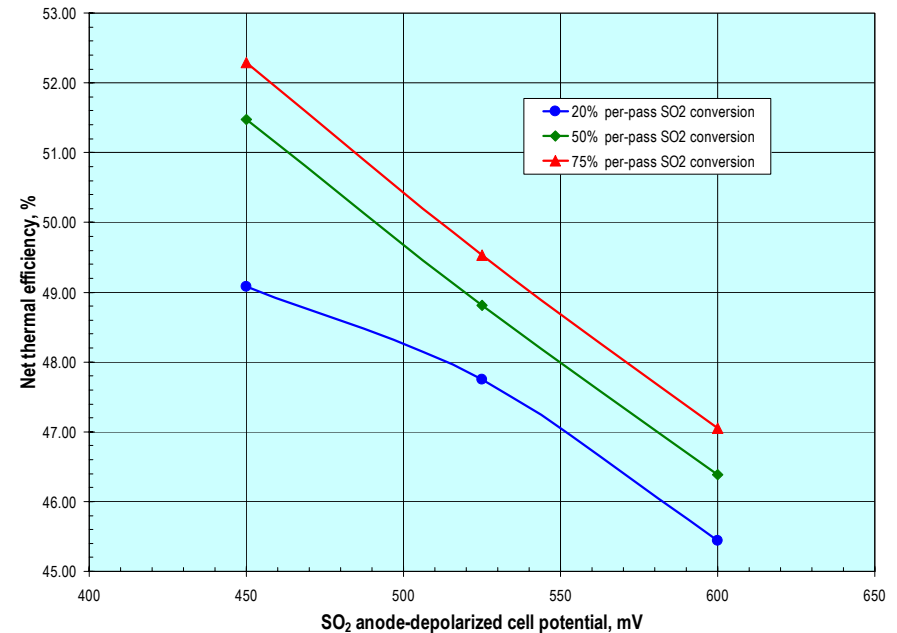
- AspenPlus flowsheet, material and energy balances, performance, heat source integration, capital and production costs
- Performance goals set for electrolyzer; test data is needed for further design optimization
- Improved acid processing scheme developed (89% Section B thermal efficiency vs. previous 75%)
- High-efficiency SO₂/O₂ separation system developed (patent pending)
- Tradeoff studies in process for electrolyzer acid feed concentration, cell temperature and pressure, and acid decomposition temperature



Tradeoff Studies

- Greatest performance uncertainty is with regard to electrolyzer efficiency
- High acid concentrations increase voltage (lower cell efficiency) but lower Section B thermal requirements
- Lower current densities reduce cell voltage but require bigger cells
- Other variables include T and P and SO₂ conversion per pass
- More experimental data is needed
- Sensitivity analysis shows overall plant thermal efficiency varies from 45.4% (20% conversion, 600 mV) to 52.3% (75% conversion, 450 mV)
- Higher temperature thermal input to Section B (>900°C) may permit greater total plant thermal efficiency

Overall HyS Plant thermal efficiency (HHV basis) vs. Cell Voltage for 900°C heat input



Baseline HyS hydrogen production costs exceed goals and are less than SI Process

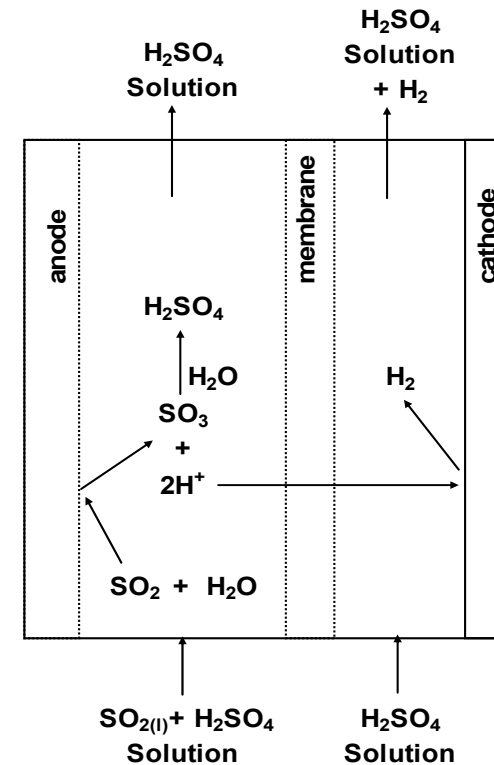
		<u>SI*</u>	<u>HyS</u>
Plant Rating	MW _{th}	2400	2400
Plant Efficiency	% (HHV basis)	52-42	48.8**
Hydrogen Output	Tonnes/Day	760-614	580
Electric Output	MWe	0	216
Reactor System Cost	\$M	1,150	1,198
Electrolyzer Cost	\$ per m ²	N/A	2000
Hydrogen Plant Cost	\$M	819	516
Electricity @ 3¢/kWh	\$M/yr	N/A	(51)
Total Annual Cost	\$M/yr	413-399	306
Net Hydrogen Cost	\$ per kg	1.65-1.98	1.60
- with O2 credit		1.36-1.69	1.31
DOE Solar Goal (2015)	\$ per kg	3.00	3.00

*W.A. Summers et al., "Centralized Hydrogen Production from Nuclear Power: Infrastructure Analysis and Test-Case Design Study, Interim Project Report, Phase A Infrastructure Analysis", US DOE NERI Topical Report, Project No. 02-160, 07/31/2004

**Current flowsheet; >50% expected.

Electrolyzer Approach

- Anode feed consists of SO_2 dissolved in sulfuric acid
- Gaseous H_2 evolves on cathode
- Cathode can be dry or contain recirculating sulfuric acid
- Original Westinghouse cells used microporous rubber membranes
- Current concept will employ Nafion membrane in MEA/PEM arrangement
- Initial testing on water only showed current densities up to 1900 mA/cm^2



SO_2 anode-depolarized electrolysis

Ambient Pressure Testing of Electrolyzer

- **Test Purposes**
 - Verify reduced cell voltages based on SO_2 -depolarization
 - Verify applicability of MEA and PEM concepts
 - Examine issues of SO_2 crossover and cell degradation with time
 - Acquire data for modeling and system scale-up
- **Experimental Status**
 - Test plan prepared
 - Awaiting completion of test facility



**Modified PEM Water Electrolyzer
(84 cm² active cell area)**

**(Manufactured by Proton Energy
Systems, Inc. with SRNL specified
materials and changes)**

Test Facility in Progress

- Design complete and all equipment on hand
- Operating plan and safety analysis completed
- Final approvals in progress
- Shakedown testing planned for mid-May



Fume Hood for installation of SO₂ anode-depolarized electrolyzer tests

Technical Issues and Concerns

- **Compatibility of MEA/PEM design with operating conditions**
- **Prevention of SO₂ crossover to cathode (i.e. sulfur deposits)**
- **Need for better data on SO₂ solubility in sulfuric acid**
- **Material selections for MEA components**
- **Electrocatalyst type and loadings**
- **Effect of increased operating pressure on SO₂ solubility and electrolyzer performance**
- **Tradeoff study on operating pressure/temperature and sulfuric acid concentration; flowsheet optimization**
- **Verification of improved SO₂/O₂ separation design**
- **Integration with SI-developed acid decomposition system**

Response to Previous Year Reviewers' Comments

- **Not Applicable**
- **This is the first year this project has been reviewed**

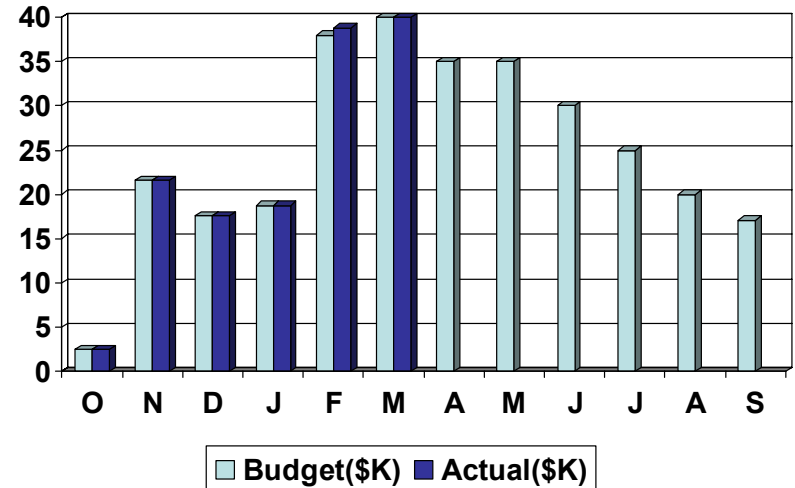
Milestone Status and Project Issues

Milestones

- **Test Plan for Small Single Cell Electrolyzer(M3) – 3/1/05 (Completed)**
- **Conceptual design for HyS including efficiency estimate(M3) -4/1/05 (Completed)**
- **Characterization Testing of H₂O-SO₂ Electrolyzer(M2) – 8/1/05 (On Schedule)**
- **Design Small Single Cell Pressurized Electrolyzer(M3) – 9/15/05 (start 6/1/05)**

Issues

- **FY06 funding needs to be substantially increased for this process to be ready for the pilot plant decision by end of FY08**



Total FY05 Funding = \$300 K

Future Plans

- **FY05 Second Half**
 - Assemble test facility and initiate shakedown testing
 - Baseline testing with water followed by water/SO₂
 - Characterization testing with various sulfuric acid concentrations and operating temperatures
 - Duration testing up to 100 hours
 - Prepare pressurized electrolyzer design
- **FY06 Proposed**
 - Design and construct pressurized (20 bar) electrolyzer and test facility
 - Perform system analysis and flowsheet improvements

Publications and Presentations

1. **W. A. Summers, “Hybrid Sulfur Thermochemical Process”, DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, September 21, 2004.**
2. **M. R. Buckner, “Hybrid Sulfur Thermochemical Process”, DOE Office of Nuclear Energy, Science and Technology, Semi-annual Program Review, Washington, DC, March 10, 2005.**
3. **M. R. Buckner et al, “Conceptual Design for a Hybrid Sulfur Hydrogen Production Plant”, prepared for DOE Office of Nuclear Energy, Science and Technology under appropriation AF38, Nuclear Hydrogen Initiative, Savannah River National Laboratory Report No. WSRC-TR-2004-00460, April 1, 2005.**
4. **M. B. Gorenssek, W. A. Summers and Mr. R. Buckner, “Conceptual Design for a Hybrid Sulfur Thermochemical Hydrogen Process Plant”, AIChE Spring 2005 National Meeting, Atlanta, GA, April 13, 2005**

Hydrogen Safety

- **The most significant hydrogen hazard associated with this project is:**

The wide range of flammability limits for hydrogen in air, from 4% by volume to 74.5% by volume. Hydrogen leaks from a poorly designed experiment could cause an invisible flame, deflagration or even detonation, potentially resulting in personnel burns or equipment damage.

Hydrogen Safety –

Our approach to deal with this hazard is:

- **SRNL requires that all laboratory work be reviewed using the copyrighted SRNL Conduct of R&D Manual. This process includes performing hazard assessments and mitigation analyses prior to the start of any laboratory work.**
- **Specific procedures for this project include:**
 1. **Operate in a well ventilated chemical hood that will maintain the hydrogen concentration well below the lower flammability limit, even with an equipment failure.**
 2. **Use components and piping rated for the pressure.**
 3. **Work with a hydrogen production rate of only two grams per hour.**
 4. **Operate using a detailed and peer reviewed Work Instruction.**
 5. **Always have at least two people present in the laboratory when work is being performed that has the potential to release hydrogen.**
 6. **Restrict access to the laboratory with a door lock and restrict access to the hood area with a railing.**